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Inclusions in Iron

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By

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INCLUSIONS IN IRON

*A Photomicrographic Study**

BY C. R. WOHRMAN

CHAPTER I

INTRODUCTION

1. An Outline of the Inclusion Problem and of the Author's Work

INCLUSIONS or enclosures in metals have early attracted the attention of scientists. Sulphide inclusions in iron were described and studied some 25 or 30 years ago by Andrews, Le Chatelier and Arnold who recorded some remarkably accurate observations on the subject. Their work was continued and supplemented by Heyn and Bauer, Stead, Law, Ziegler and Matveieff, and, in more recent years, by Levy, Röhl, McCance, Hibbard, Comstock, and a number of other investigators.

The subject of inclusions appears, nevertheless, to have received less attention than it deserves. The genesis of inclusions, their characteristics and habits, on the one hand, and their effects on the useful properties of metals, on the other, are less well understood than would appear from a casual acquaintance with the subject.

The reason for this lies, undoubtedly, in the great complexity of the subject requiring for its study not only ingenuity and skill, but also precision equipment and laboratory facilities of the highest order. The subject is, furthermore, so broad as to require for its understanding the correlation and assembling of a great variety of detailed data secured from a variety of diverse sources and experiments.

A comprehensive study of inclusions in iron and steel, for example, implies not only a study of the finished product but a detailed investigation into the entire process of making the product

*From a thesis by C. R. Wahrman submitted to Harvard University in partial fulfillment of the requirements for the degree of Doctor of Science in Metallurgy. The experiments were conducted in Professor Sauveur's laboratory. The paper is divided into five chapters. Manuscript received January 4, 1928.

as well. To begin with, there is the ore, the pig iron, the scrap, the furnace lining—all of which supply inclusion-forming material. A variety of slags are produced in commercial practice, every one of which is a most complicated physico-chemical system. The molten metal itself, containing a variety of elements, is a system of great complexity. The effect of temperature and of the furnace atmosphere have to be considered. The viscosity of the metal and the slag, the phenomena of surface tension and of diffusion are factors of importance. The temperature of pouring, the varying practice of ladle additions, the speed of solidification and of subsequent cooling have an influence. These factors are, furthermore, closely intertwined and interdependent in their importance and effects. The study of any or all of them is troublesome on account of the high temperatures involved and the difficulty of separating the variables present.

A study of the inclusions already formed, such as found in commercial iron and steel, is also far from simple. Here the minuteness of the inclusions makes qualitative tests a task, and, in microscopic work, necessitates the use of high magnifications coupled with careful preparation of the samples.

All these difficulties constitute, of course, no valid excuse for neglecting the study of inclusions. Specifications for steels are becoming continually more rigid and standards more and more exacting. Can we, under the circumstances, neglect the influence of inclusions? Must we not issue "inclusion specifications" analogous to the specifications issued for the case of alloy-forming impurities? Recommendations to this effect have, indeed, already been made.

But, before we can formulate useful specifications, we must know the facts. The main issues of the problem of inclusions are:

- I. What is the influence of inclusions on the useful physical properties of the metal? In particular, what is the influence of:
 1. The number of inclusions
 2. Their size and shape
 3. The kind of inclusion.
- II. How can we govern inclusions? An answer to this implies:
 1. The ability to identify inclusions
 2. The knowledge of inclusions, i. e., of:

- (a) The conditions leading to their birth-sources
- (b) The conditions surrounding their birth-formation
- (c) Their habits
- (d) Their friends and enemies—conditions favoring retention and elimination.

The first of these issues is largely a problem in the strength of materials, the second one of physical chemistry.

The present research is concerned, primarily, with the second question, i. e., the study of how to govern inclusions, the problem being approached by a microscopic inquiry into the characteristics and the behavior of the more important inclusions found in iron. The present research is, thus, essentially a photomicrographic study of inclusions, limited to the case of inclusions in iron.

In particular, the present research concerns itself with a study of the characteristics and behavior of the inclusions created in iron by oxygen, sulphur and manganese, i. e., the inclusions ordinarily referred to as FeO, MnO, FeS, MnS, and their combinations. The study of silicates forms a subject by itself and could not be taken up in requisite detail.

The first chapter of the present paper is of an introductory nature. The methods used for making artificial known inclusions desired for the studies are described; the preparation of specimens, in particular the methods of polishing for inclusions, are considered next; finally, the technique of microscopic examination is dealt with.

The oxide, sulphide, and oxide-sulphide inclusions are then described in Chapters II, III and IV, respectively. Their appearance and typical occurrence is noted in each case, as well as their etching characteristics in the more common reagents used in metallographic work. Particular attention is paid to the constitution of the inclusions and the much disputed questions relating to their origin and behavior.

Chapter V serves to summarize and discuss the evidence thus obtained, and to correlate it with accepted theories and hypotheses about the nature of inclusions. The sources of inclusion-forming materials, the status of inclusions in the molten metal and their formation are discussed, and the conditions governing their size,

shape and distribution outlined. The behavior of inclusions, their occurrence at grain boundaries and preferential association with the pro-eutectoid elements, is discussed next. The problem of identification of inclusions is also touched upon. Desirable modifications and changes in Campbell and Comstock's "Method for the Identification of Non-Metallic Inclusions in Iron and Steel" are suggested. The influence of inclusions on the useful properties of metals is then briefly examined. The phenomenon of red-shortness receives especial attention and a new explanation for it is offered. The chapter is concluded with a brief reference to the problem of elimination of inclusions.

2. *The Preparation of Artificial Known Inclusions*

Inclusions, in most instances, have been studied in their natural state, i. e., in the form in which they appear in commercial iron and steel. Such studies are hardly capable of yielding the specific information that is essential for a satisfactory solution of the problem of inclusions.

Inclusions, ordinarily, appear in metals in the form of tiny globules and streaks which oftentimes, at ordinary magnifications, are barely visible. It is easy to understand that the effects of sundry chemical and other tests can be judged, on that account, only with difficulty. Unless we are well acquainted with the specific characteristics of known inclusions we cannot hope to identify and to interpret unknown inclusions. It is necessary, therefore, at the outset, to prepare artificial known inclusions and to study them first.

The idea of making artificial inclusions is not new. Matveieff¹ prepared a complete set of such inclusions by filling a wrought iron tube with the necessary inclusion material, heating the tube to about 2370 degrees Fabr. (1300 degrees Cent.) and forging it. This method has the serious drawback of not reproducing the conditions under which inclusions actually form. The extent to which the materials that make up inclusions react, and the way in which they react, depends to a great extent on the temperature at which the reactions take place. Representative artificial inclusions can, therefore, be prepared only by actually melting the metal and the

¹*Revue de Metallurgie*, 1910, p. 447 et seq.
Revue de Metallurgie, 1920, p. 736 et seq.

inclusion-forming materials together. This latter method has been used by Arnold,² Röhl,³ and a number of other investigators.

In the present research care was taken to avoid contamination of the melt by extraneous substances—a precaution which was not always taken by earlier workers. Electrolytic iron was used throughout, and chemicals of highest purity only were employed. An Arsem furnace was used for the preparation of the melts.

The corrosive action of some chemicals, notably of iron oxide and manganese proved detrimental to both the alundum (fused alumina) crucibles employed, and the purity of the melt. In order to avoid this and, at the same time, to prevent the escape

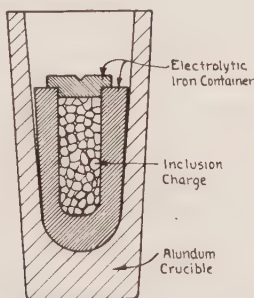


Fig. 1—Diagram Illustrating Crucible in Which Sample Melts Were Made.

of the more volatile charges (sulphur, for example) the melts were prepared in securely closed containers of vacuum-melted electrolytic iron placed, in turn, into the alundum crucibles. (See Fig. 1). The charge, then, would usually be absorbed by the iron while the latter was still solid or semi-solid and the crucible upon final melting was exposed merely to the corrosive effect of the alloy, which proved to be negligible. This arrangement had the further theoretical advantage that impurities insoluble in the iron (and, as is usually the case, having lower melting points than iron) would undisturbedly⁴ melt into one lump inside the container and float bodily to the top of the melt upon fusion of the enclosing walls.

All “sulphide” melts were done in vacuo, most of the “oxide” and “oxide-sulphide” melts in air. In either case the temperature

²*Journal*, Iron and Steel Institute, 1914, I, p. 396 et seq.

³*Carnegie Scholarship Memoirs*, Iron and Steel Institute, 1912, p. 28 et seq.

⁴There is no stirring action in the Arsem furnace.

was raised gradually, the melting point of the charge being reached, ordinarily, in 30 to 40 minutes. The metal was kept molten for at least 5 minutes during which period the temperature continued to rise.⁵ Ample opportunity was thus given for such supposedly agglomerated inclusion material as was insoluble in the metal to float to the top. Next, the temperature was gradually lowered, at first slowly, so as to permit slow solidification and unrestrained segregation, then more rapidly. Normally, the charge was cooled to a dull red in the course of 30 to 40 minutes.

In the case of air-melts it was found usually convenient (and sometimes necessary to supply additional inclusion-forming material after the melting of the original charge. This was accomplished by dropping pellets (about 5 millimeters in diameter) onto the surface of the molten metal. In all such cases the time required for the melting or absorption of the added material was noted, and the metal was kept molten correspondingly longer.

The prepared ingots weighed, on the average, about 60 grams (2 ounces). This size, although dictated to a certain extent by the capacity of the furnace, was chosen for the convenience in the further preparation and study of the specimens. The ingots, in most cases, were sawed into halves, longitudinally; one half was polished for microscopic examination, and the other half reserved for chemical analysis. A complete section of each ingot was thus secured for examination at a minimum of labor.

Accurate chemical analyses of the melts were kindly made by the well-trained staff of the chemical laboratory of the American Rolling Mill Company. These analyses, together with other essential information about individual melts, are given in Chapters II, III and IV.

3. Polishing for Inclusions

The preparation of the samples for microscopic examination was a tedious task. Polishing of specimens for microscopic work is distinctly an art, and polishing for inclusions a very special art. A "science" of polishing is as yet not in existence.

The nature of polish has been studied by a number of investi-

⁵Facilities for reliable measurements of the temperature in the vacuum furnace were, unfortunately, lacking.

gators,⁶ and appears to be fairly well understood. A rather sharp line is usually drawn between the action of abrasives fixed to a rigid base, grinding, and the action of finer "loose" abrasives used on a wetted cloth. The former is taken to imply cutting or ploughing of grooves, the latter, flow, with the attendant generation of amorphous metal. In the opinion of the writer the difference between the two processes is one of degree, not of kind. Flow of the metal, at any rate in the case of soft metals, takes place on grinding just as surely as it does on polishing proper. It is a logical consequence of the reaction of the metal to the stresses imposed upon it, and these stresses differ only in degree.

In the last analysis, grinding and polishing of a surface imply "working" that surface. Forces ever-changing in magnitude and direction are exerted on the surface layer of the metal, the stresses imposed being in excess of the strength of the metal, or its resistance to deformation. Mechanical twinning⁷ will take place, followed by "fragmentation," which, in the writer's opinion, implies merely the substitution of an extremely fine grain for the pre-existing coarser grain. The resulting very fine-grained aggregate is, naturally, much harder than the original metal and represents the utmost in strength and resistance that the metal is able to command against the forces of polishing. The assumption of an amorphous phase is superfluous. In fact, recent X-ray studies have shown that heavily polished surfaces of metals gave no evidence of an amorphous state.⁸

The process of polishing appears to be a simple one requiring merely patience, especially in the case of pure iron and other soft metals. On attempting to analyze the process, the complexity of the problem becomes at once apparent.

Indeed, what basic facts are known to us that could guide us intelligently in the choice of the particular cloth and powder

⁶Robert Hooke, "Micrographia". Observation II.
Lord Raleigh, *Proceedings*, Royal Institute, 1901, 16, 563.
G. T. Beilby, *Proceedings*, Royal Society, 1903, 72, 218, 226.
Philosophical Magazine, 1904, 8, 258.
Faraday Society, June, 1904.
Journal, Society of Chemical Industry, 1903, 22, 1166.
Journal, Institute of Metals, 1911, VI, 2.
F. Osmond and G. Cartaud, *Revue Generale Sciences*, 1905, 16, 51.
W. Rosenhain, "Physical Metallurgy", 2nd edition, Part I, Chapter II.

⁷See L. B. Pfeil, "The Deformation of Iron," Iron and Steel Institute, *Carnegie Scholarship Memoirs*, 1926, p. 320 et seq.

⁸R. J. Anderson and J. T. Norton, "X-Ray Evidences vs. the Amorphous-Metal Hypothesis," *Transactions*, American Institute of Mining and Metallurgical Engineers, January, 1925.

to be used for polishing a given metal or in the choice of the speed of the wheel, the proportion of water in the polishing mixture, or the amount of the mixture to be applied? To those who know, the sensitiveness of a good polish to these and related variables need not be emphasized. But more than that, what are the fundamental considerations that led us to assume the combination of a cloth, an oxide powder, and water to make the ideal polishing combination? Perhaps we should use a metal base for the powder—lead, for example—and lubricate it with oil,⁹ or, perhaps, polish with a paraffin disk lubricated with a soap solution?¹⁰ And so on, ad infinitum.

The experience of earlier workers in the field of metallography and related fields is available to guide us. But experience based, as it is, on rather incomplete trials alone, and not substantiated by analytical experiments, nor logical deductions, cannot convince anyone of offering the best solution.

The established experimental facts, and attendant fundamental considerations, as they appear to the writer, are summarized below. The main items detrimental to a good polish are:

I. Too deep a flowed layer.

II. Pits.

I. The depth of flow is a function of:

1. The stresses acting during polishing:

- | | |
|------------------------------|---|
| (a) The greater the pressure | } the greater will be the forces exerted per unit area of the surface polished. |
| (b) The greater the speed | |
| (c) The finer the powder | |

2. The plasticity or softness of the metal:

- (a) The more readily the metal yields the more flow will be induced by a given stress.

3. The polishing combination:

- (a) Character of abrasive and lubricant (influence rather problematical).

⁹Promising experiments with this combination are being conducted in Professor L. C. Graton's Laboratory at the present.

¹⁰Recommended by R. G. Guthrie, TRANSACTIONS, American Society for Steel Treating, March, 1925.

(b) Manner in which abrasive is held:

Abrasives attached to a rigid base induce less flow than those used in "loose" form.

II. Pits, irrespective of the character of the material polished, are induced primarily by:

1. Abrasives applied in the "loose" form, especially the grades used for intermediate polish; the effect is aggravated by a fluffy soft cloth and high speed.
2. Vibration of the polishing wheel and related causes which imply sudden changes in the polishing stresses.

The main requisites for obtaining a good polish are therefore as follows:

1. The use of abrasives fixed to a rigid base.
2. A "gentle touch" and "slow speed" throughout all operations, especially in the case of the softer metals.
3. Polishing equipment free from vibration.

Polishing for Inclusions

The preparation of a metal for the microscopic examination of inclusions contained in it implies first and foremost the preservation of these inclusions.

This seems too obvious a fact to need mentioning, yet, judging from some of the pictures appearing in the literature, this fact is not generally understood. Fig. 2 is a reproduction of a photomicrograph published with a well-known paper on inclusions in a well-known journal. It purports to be a photomicrograph at $\times 1000$ of oxide inclusions. It is a picture of a group of small pits surrounding a larger pit. Numerous instances of this sort could be cited. Holes should never be called inclusions even if they are suspected to have contained inclusions.

Inclusions, whether they appear in the metal in the form of globules, as elongated streaks, or as angular bodies, have in all and every case clear-cut and well-defined outlines. Fig. 3 shows the appearance, under the microscope, of properly polished and preserved iron-oxide inclusions.¹¹ The reader is invited to compare

¹¹The specimen was prepared by W. McGohan of the research department of the American Rolling Mill Company.

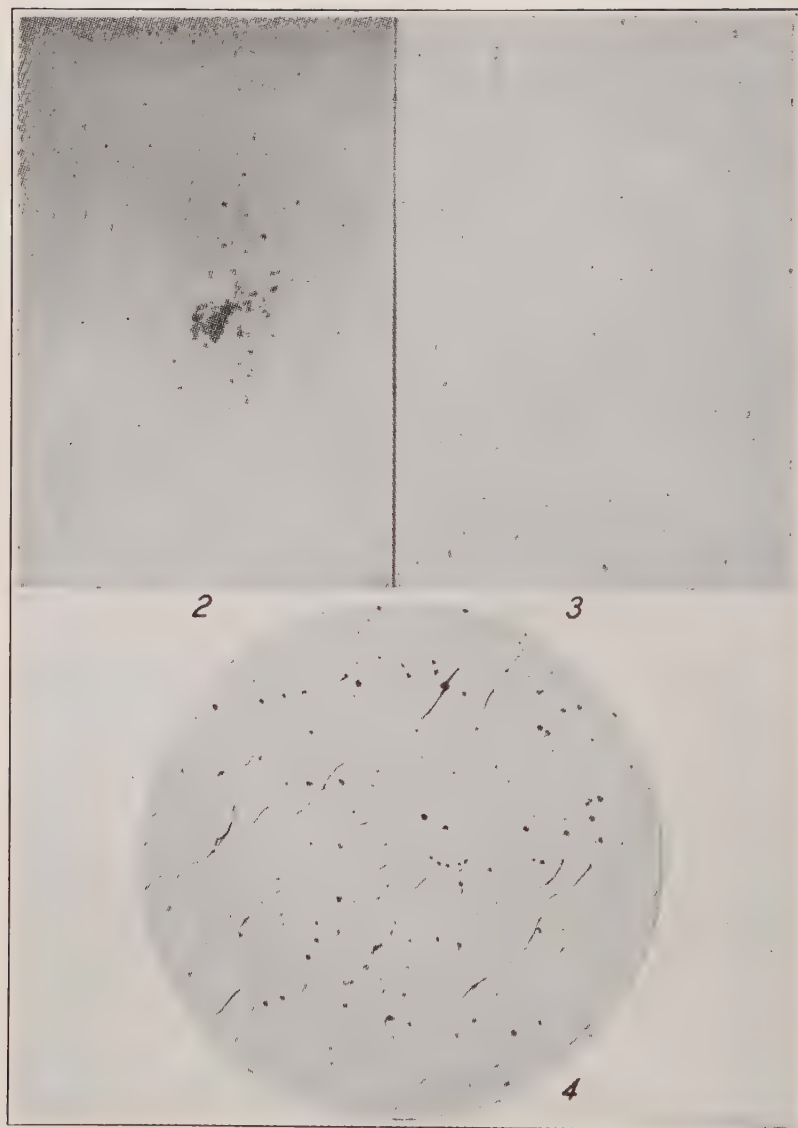


Fig. 2—Reproduction of a Photograph of "Oxide Inclusions" Published in a Well-known Paper. Actually it is a Large Pit Surrounded by Smaller Pits. $\times 100$. Fig. 3—Appearance of Properly Polished Oxide Inclusions. Note the Definite Outlines and Coloration. $\times 100$. Fig. 4—Polishing Pits Simulating Inclusions in Vacuum-melted and Lightly Etched Electrolytic Iron. $\times 100$.

the appearance of these inclusions with that of the spots of Fig. 4. The latter are pits in an improperly polished piece of vacuum-melted electrolytic iron, essentially free from gases and inclusions of any sort.

The preservation of inclusions is difficult. Some¹² believe that there is no cohesion between the metal and inclusions and that the latter are obliged to drop out whenever the plane of the section lies below their maximum diameter. According to the observations of the author this is not the case. A definite, though weak, cohesion exists; at any rate in metals in the cast or forged condition.

It is the pitting action of polishing that causes the trouble. Pitting is noticeable already in the case of a plastic metal; it is only natural that it should prove detrimental to the brittle inclusions and the weak joints between the metal and inclusions.

Realizing this the author endeavored to reduce pitting to a minimum. At first F. F. Lucas' method¹³ was used. The results were not perfect, yet quite satisfactory when Lucas' specifications were followed exactly, and the polishing carried out on laps with a direct drive. The friction drive laps, with their inherent vibration, were found to be detrimental to inclusions, no matter how carefully the specimens were polished otherwise. Further work showed that the intermediate alundum lap was harmful to the inclusions, and ways were sought to avoid it altogether. A description of the various trials and re-trials will be spared to the reader.

A more or less satisfactory solution was finally found in a method which practically disposes of the use of "loose" abrasives. Preliminary hand grinding on emery papers was followed directly by final polishing on a vibrationless disk covered with a billiard cloth of dense weave to which jeweler's rouge in cake form was applied.¹⁴ This rouge, when spread on the wheel, becomes firmly lodged in the close weave of the cloth and does not float around in the water as polishing powders usually do. We thus approximate to the case of an exceedingly fine abrasive attached to a rigid base. This behavior of the rouge is explained by the fact that the binder employed in making the cake, while soluble in benzene, xylene, chloroform, and related organic liquids, has a repelling

¹²J. O. Arnold, *The Metallographist*, 1900 p. 273-74.

¹³Appendix III of Albert Sauveur's "Metallography", 3rd edition, 1926.

¹⁴The polishing combination: billiard cloth and cake rouge, was devised by W. McGohan of the American Rolling Mill Company.

action on water. Water, in fact, does not wet the rouge-covered disk, and acts merely as a lubricant.

A detailed description of the steps employed by the author in polishing for inclusions follows:

1. Very light grinding on a fine emery wheel.
2. Flattening of the surface by hand grinding on "India" oil-stone (coarse).
3. Grinding by hand on French emery paper beginning with No. 1 and finishing with No. 0000. No oil or kerosene should be used—at least not on the final papers.

The pressure exerted should be very slight on the coarser grades and practically nil on the finer.

4. Polishing on a disk covered with a good grade of moistened billiard cloth and charged with rouge by pressing a cake of finest jeweler's rouge against the revolving wheel. Water is dropped at a constant rate on the wheel which is revolved at about 700 revolutions per minute. If the rouge sticks to the specimen the amount applied is too heavy, or else there is not enough lubrication by water. In the beginning of the operation a moderate pressure can be exerted on the specimen which is to be moved about on the wheel and rotated to insure an even polish. Toward the end of the operation, which should be completed in 5 to 10 minutes, no pressure at all should be used. It is imperative that the wheel be vibrationless. (The author used a belt-driven ball-bearing machine manufactured by a well-known concern).
5. Washing of the specimen in benzene and alcohol and touching it for half a minute or so to a very slowly (100 revolutions per minute) revolving lap of kitten's ear cloth charged with a paste of finest magnesium oxide. This operation disposes of traces of rouge adhering to the specimen and adds to the quality of the polish.

If due care was taken in all operations the inclusions were found to be preserved in perfection. Whenever the time was limited, however, and the materials inferior,¹⁵ the results suffered correspondingly. The amount of flow, caused by the rapidly revolving rouge wheel, was often found to be in excess of the allowable

¹⁵Hubert emery paper, in particular, was found to be of an unsatisfactory quality of late.

limit, especially when the finishing on emery paper was imperfect. This did not interfere, however, with the study of inclusions.

The example of the rouge wheel serves to underline the merits of a "fixed" abrasive and suggests a way of preparing such abrasives for fine as well as intermediate polishing.

4. *Microscopic Examination of Inclusions*

Magnifications Used. The inclusions met with in commercial iron and steel are usually small. A maximum diameter of 0.01 millimeters is seldom exceeded except in the case of inclusions markedly elongated by hot work. The structure of individual inclusions, accordingly, can be seen with any certainty only at high magnifications. The effect of etching treatments on inclusions, similarly, can be observed clearly and unmistakably only at relatively high powers. On the other hand, if the distribution of inclusions is studied, or their relative abundance, low magnification must be used.

The author found the following magnifications convenient:

1. $31\frac{1}{2}$ —for studying the relation of inclusions to the existing grains and to the primary dendritic grains of the iron.
2. 100 —for a general survey of the distribution, predominant form, and "density" of inclusions.
3. 500 —for observing etching effects on individual inclusions and groups of inclusions.
4. 2500—for detailed study of the structure of complex inclusions.

Each specimen was examined successively at each of the magnifications stated.

Facts About Photomicrography. It will, perhaps, be helpful, in this connection, to point out some of the facts about low and high magnifications in photomicrography that have not been properly emphasized by earlier investigators. They can be stated as follows:

1. If two or more constituents are present in a metallographic specimen their differences become apparent:
 - (a) on account of inherent differences in color and brilliancy

- (b) on account of artificial color differences induced by etching and tinting treatments
 - (c) on account of a relief effect created by differential dissolution of the constituents by etching reagents, or by polishing.
2. Relief causes shadows which are the more confusing the higher the relief, the finer the structure and the lower the magnification used. (Pearlite is an example—see Technical Publication, No. 14, American Institute of Mining and Metallurgical Engineers, September 1927, p. 9).
 3. Differences due to coloration appear the more pronounced the higher the magnification used.

In other words, while contrasts due to relief are diminished, true color differences are greatly enhanced by high magnifications.

How to Distinguish Inclusions.—The bearing of these facts on the microscopic study of inclusions is obvious. High magnifications will not only facilitate distinction on the basis of faint differences in color and shade, but will unmistakably point out whether or not we are dealing with an inclusion or with a pit.

Whenever a light-colored inclusion is observed at low powers, say $\times 100$, we can be sure that it is an inclusion. If a black "inclusion" is seen, however, it may be an inclusion, but it may also be a hole appearing dark due to a shadow effect.

Fig. 5 exhibits an assembly of such dark "inclusions." Their outlines are clear cut and definite, their shape is rounded and typical for inclusions, their color is dark, they are, furthermore, not reduced by hydrogen, nor attacked by sodium pierate,—they must, on the basis of our standards for identification, be silicates. It is possible that they were silicates. We do not know, because at the present they are just holes. Fig. 6 shows two of these holes at a magnification of $\times 500$. Beautiful interference rings are seen, formed by reflection of the light from the walls of the accurately spherical depressions. No material inclusion, of course, is capable of producing such light effects unless, indeed, it be a perfectly transparent glass. The possibility of such glasses occurring as inclusions is remote; still, in case of doubt, a scratch test will tell the story.

In some exceptional cases the shape of the hole is such as to simulate an inclusion even at the higher magnifications. The large



Fig. 5—Are the Black Spots Inclusions? Mag. $\times 100$. Fig. 6—View of Two of the Spots of Fig. 5 at $\times 500$. They are Spherical Holes. Fig. 7—Note the Larger "Inclusion". $\times 500$. Fig. 8—Same as Fig. 7 Viewed with the Objective Focussed Toward the Bottom of the "Inclusions". The Light Spot Which Appears Indicates a Hole. $\times 500$.

"inclusion" of Fig. 7 is an example. The final test, in such cases, consists in focusing on the bottom of the "inclusion." If it is an inclusion it will remain dark—merely fading in clearness,—if it is a hole, a bright area will appear when the lens is focused on the bottom (Fig. 8).

This test of changing the focus can be applied conveniently

while the specimen is being examined at low powers, and gives then a good idea of the relative number of inclusions that were pitted out in polishing.*

Contrasts in Photomicrographs.—Attention should, perhaps, be called to the fact that photomicrographs, generally, do not reproduce the actually existing contrasts in a faithful manner, unless special care is taken to this effect. The degree of contrast secured in the final print is not only a function of the contrast of the negative, but to a large extent of the grade of paper used and of the time of exposure and development. The degree of contrast of the negative, in turn, depends not only on the contrast of the actual structures photographed, but on the color filter employed, kind of plate used, time of exposure, manner of development, etc.

In the present work, "Wratten M" plates were used and "Azo" printing papers. Whenever desirable, the author endeavored to reproduce the existing contrasts as faithfully as his judgment and working conditions permitted.

*Observations made after the completion of the present paper have shown that the occurrence of transparent inclusions is by far not as remote as might be inferred from the statements made. Silica and silicates are often semi-transparent or translucent and can, at times, be recognized by this feature.

The change of focus test will, therefore, show up not only pits but both pits and transparent inclusions. To distinguish between transparent inclusions and cavities, a scratch test might be employed. It will be simpler, however, to pass judgment on the basis of the outlines exhibited by the spot. If the outlines are clean and sharp (as in Figs. 6 and 7), we are fairly sure to deal with an inclusion; if they appear smeared and indistinct, we have a pit or a cavity. Holes can exhibit sharp outlines only when the contained inclusion has dropped out in the very last stages of polishing; and cases of this kind are exceptional.

CHAPTER II

OXIDE INCLUSIONS (AND SILICATES)

I. Review of Existing Knowledge

THE present chapter deals primarily with iron oxide and manganese oxide inclusions in iron.

A vast amount of work has been done on these oxides and on their equilibrium relations in steel making processes. Oxides of iron, in particular, have been investigated in great detail. An idea of the magnitude of this work can be gained from the list of references appended to this chapter,¹⁶ the list being far from complete. The surprising degree of confusion existing in this literature and the lack of agreement in respect to many important and fundamental points serves to emphasize the complexity of the problem and the difficulties encountered in experimentation. No attempt will be made (and cannot be made within the scope of this work) to go into these problems in any detail. It will be helpful, however, to review briefly such data as are most important for the problem of inclusions.

Iron Oxides.—Both ferric oxide, or hematite (Fe_2O_3), and ferroferric oxide, or magnetite, occur naturally and are well-known. Both exhibit polymorphism as was shown by Sosman (14). At temperatures above 2010 degrees Fahr. (1100 degrees Cent.) these two oxides form a continuous series of solid solutions (20,41); the extent of solid solubility at lower temperatures is not definitely known; it appears, however, to be small.

Ferrous oxide, FeO , has never been isolated in the pure state, chemical analyses revealing always the presence of some Fe_2O_3 . Hilpert and Beyer (25) ascribed this to the formation of solid solutions between FeO and Fe_3O_4 . As pointed out by Eastman (29), the presence of Fe_3O_4 in carefully prepared FeO could equally well be accounted for by the instability of FeO , with respect to Fe_3O_4 and Fe , below some definite temperature. According to this conception ferrous oxide prepared at a higher temperature would react partly on cooling, to form Fe_3O_4 and iron:

¹⁶Numbers in brackets refer to the list of references appended to this chapter, not to the list at the end of the paper.



The instability of FeO at low temperatures has been verified by Chaudron (13). The existence of solid solutions between FeO and Fe_3O_4 has, however, also been verified,—by Matsubara (42),—who found Fe_3O_4 to be soluble to a limited extent in FeO at temperatures below 2010 degrees Fahr. (1100 degrees Cent.). It is suspected that a continuous series of solid solutions exists at higher temperatures. A suboxide of iron, Fe_3O , is believed, by Schenck (41), to be stable in the presence of FeO and Fe_3C at relatively low temperatures.

The question of solubility of the oxides in iron merits especial attention. Indeed, the entire problem of elimination of inclusions hinges on the question whether inclusions are suspensions in the molten metal, or whether they are precipitated from solution on solidification; or even later, on cooling of the already solid metal. Only the ferrous oxide, FeO, needs to be considered in this connection since the higher oxides are reduced, in the presence of molten iron, to FeO.

Ferrous oxide, until recently, was held by many metallurgists to be insoluble in iron, despite the fact that the oxide content of the metal bath was observed to be a function of the composition of the slag and of the temperature. This is, surely, indicative of an equilibrium relation that could not be brought about by mechanically suspended matter.

Le Chatelier and his school were, perhaps, the first to advocate the solubility of oxygen in iron. According to Le Chatelier, oxygen is soluble even in solid iron producing, on segregation, the dendritic heterogeneity of cast steel and the banded structure observed in forged material. This view has been contested by Stead who has conclusively shown that phosphorus, and not oxygen, is responsible for the observed segregation phenomena.

In 1915, W. Austin (45), on the basis of a study of artificially prepared oxygenated alloys, concluded that, "it is conceivable that the oxide is soluble in molten iron, but is rejected on solidification."

In 1918, A. McCance (46), on the basis of a study of open-hearth reactions, stated that, "all the evidence is favorable to the view that FeO is in solution in liquid steel."

Finally, in 1924, Tritton and Hanson (47) succeeded in preparing containers capable of holding molten iron oxide, and were

thus enabled to study the iron-oxygen system. They found that molten iron dissolves up to 0.21 per cent oxygen while solid iron can hold in solution only some 0.05 per cent. The solubility of iron oxide in iron is further substantiated by the researches of Eastman and Evans (33), Schenck (41) and others who investigated the iron-oxygen-carbon and iron-oxygen-hydrogen systems.

Additional data of interest about FeO are summarized in the table below where they can be compared with the corresponding data for MnO.

| | Mol wt. | Crystal system | Melting Point | Density (20°C) | Heat of Formation Cals. per gram atom |
|-----|------------|--------------------|------------------|-------------------|--|
| FeO | 71.84 | Cubic NaCl type | 1420°C | Unknown | Oxygen 56 |
| MnO | 70.93 | Cubic NaCl type | 1650°C | 5.18 | 73 |

Manganese Oxide.—Of the great number of manganese oxides only MnO is of interest from the inclusion standpoint. A mineral of this composition, manganosite, is known to exist, but is, however, relatively rare.

In iron, MnO is shown to be formed according to the reaction



in the course of “deoxidation” by manganese. This reaction is reversible and proceeds in a manner dependent on the concentration of the factors involved and on the temperature, i. e., until equilibrium is established. The equilibrium conditions have been studied by a number of investigators (24, 37, 38, 39).

The solubility of MnO in molten iron has not been determined. From a consideration of the equation given above it would appear that MnO must be soluble in iron, even if only to a small extent. Indeed, manganese and FeO are known to be soluble in molten iron; the existence then, of equilibrium relations of these factors with MnO, in the liquid bath, proves the solubility of MnO in that bath.

Methods for identifying MnO (and FeO) inclusions have been given by a number of investigators (43, 46, 50). It is further generally advocated that MnO inclusions are less objectionable than inclusions of FeO. One is thus led to believe that inclusions of MnO have been definitely identified in iron and steel, and that such inclusions have an existence apart from FeO inclusions.

S. L. Hoyt (52) points out, however, that "MnO as a foreign inclusion has never been identified." He attributes this to the similarity in appearance of MnO and MnS and the consequent possibility of the oxide having been mistaken, at times, for the sulphide which is so frequently described.

2. Experimental Melts

Table I summarizes the information about the experimental oxide-bearing alloys prepared by the writer.

Table I
Oxide Experimental Melts

| Melt | Charge (grams) | To Yield, Per Cent | Chemical Analysis, Per cent | Remarks |
|------|---|--|-----------------------------------|---|
| 0-1 | El. Fe 68.02 Fe ₂ O ₃ 0.30 68.32 | Fe 99.87 O ₂ 0.13 | | Heated slowly in vacuo to about 1400 degrees Cent. (3 hours); the crucible then cracked and heating was discontinued. The specimen was allowed to cool in vacuo. |
| 0-2 | El. Fe 71.2 Fe ₂ O ₃ ? | | | Melted in air; 0.8 gr. of Fe ₂ O ₃ were charged in the container and an unknown quantity dropped into the crucible after the metal had melted. |
| 0-3 | An ingot iron crucible was heated in vacuo with a mixture of 70 grams of electrolytic iron and 30 grams Fe ₂ O ₃ to about 1400 degrees Cent. and slowly cooled. | | | |
| 0-4 | El. Fe 53.5 Mn ₂ O ₃ 4.0 57.5 | Fe 93.05 Mn 4.85 O ₂ 2.10 | Mn 0.300 | Melted in air. Of the oxide charge 1.7 gr. were added in the form of pellets dropped into the crucible after the metal had melted. The charge solidified quietly. |
| 0-5 | El. Fe 62.35 Mn ₂ O ₃ 2.05 Fe ₂ O ₃ 2.20 66.60 | Fe 95.94 Mn 2.14 O ₂ 1.92 | Mn 0.087 | Melted in air. Of the oxides 0.9 gr. was added in the form of pellets. Solidification was accompanied by evolution of gases. |
| 0-6 | El. Fe 52.90 Ferric Silicate 1.50 54.40 | | Si 0.056 | Melted in vacuo. |
| 0-7 | El. Fe 53.90 Mn Silicate 0.95 Fe Silicate 0.65 55.50 | | Mn 0.50 Si 0.020 | Melted in air. Several pellets of a mixture of Fe- and Mn-silicate were dropped on the top of the melt and were well absorbed. The crucible near the top was slightly corroded. |

3. Iron Oxide Inclusions

The melt O-1 was intended to yield pure iron oxide inclusions with which the writer was desirous to acquaint himself thoroughly before taking up the study of other inclusions. At the time, only

a rather poor grade of crucible was available in the laboratory, necessitating a very gradual and slow heating. This precaution was taken, yet the crucible cracked on reaching (after 3 hours heating) a temperature of about 2550 degrees Fahr. (1400 degrees Cent.). Heating was then discontinued and the charge allowed to cool in vacuo. The electrolytic iron container was found to have shrunk around the oxide-filled hole exhibiting upon sectioning (and polishing) the shape illustrated in Fig. 9. The hole had welded up in a perfect manner, no sign of porosity being discernible even at high magnifications. And, curiously, not a sign of the oxide could be found, although the quantity charged was in excess of the amount reported to be soluble in solid iron. The oxide, clearly, had left the container diffusing (upon reduction to FeO) through the iron and dissociating in vacuo. This experiment substantiates the solubility of iron oxide in iron and serves to caution against annealing in vacuo when the effects of a given oxygen content in iron are to be studied.

The melt O-2 being the second melt was prepared in air and exhibited the typical gray inclusions of FeO, illustrated in Fig. 16. These inclusions were found to be uniform in appearance with no indication of a duplex structure, and were distributed fairly uniformly throughout the ingot. The inclusions resisted effectively etching attempts with dilute nitric acid, chromic acid, boiling sodium picrate and boiling potassium hydroxide, it succumbed, however, to a saturated solution of stannous chloride in alcohol. It appeared, therefore, that the systematic "Method for the Identification of Non-Metallic Inclusions in Iron and Steel" of Campbell and Comstock led to correct results in this instance.

Sulphur printing¹⁷ was also tried. This treatment affected some of the smallest inclusions to a slight extent, but had no pronounced effect otherwise.

Magnetite Inclusions.—In the course of a parallel study of inclusions in ingot iron the writer observed typical iron oxide inclusions carrying (usually in their middle) tiny crystals of a dark gray constituent. (See Fig. 14.) These crystals were unfortunately

¹⁷Sulphur printing was used by the author throughout the work on inclusions as a convenient supplementary test. "Azo" printing paper was soaked in a 2 per cent H₂SO₄ solution, placed on a glass plate and the polished specimen, previously wetted, pressed firmly against the paper. The time of contact, unless specified otherwise, was 20 seconds. Since the specimens had a tendency to tarnish somewhat in the course of this procedure, sulphur printing was usually followed by a very slight "touching up" on the magnesium oxide lap. This restored the brilliancy of the polish without diminishing the etching effects of the treatment.

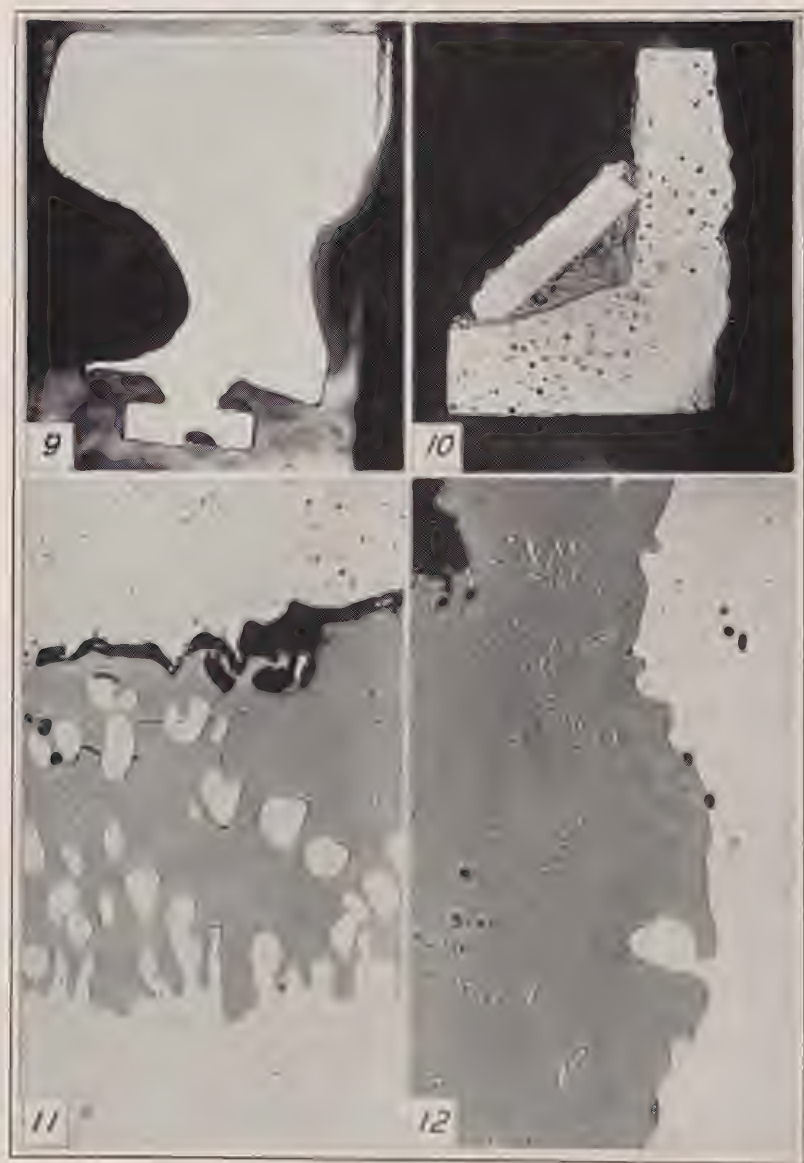


Fig. 9—Cross Section of Melt 0-1. The Hole Has Welded up in a Perfect Manner. Enlarged $\times 2$. Fig. 10—Section Through Melt 0-3 Showing Part of the Ingot Iron Crucible, a Piece of Electrolytic Iron, and Fused Iron Oxide in Between the Two. Enlarged $\times 2$. Fig. 11—Interpenetration of Oxide and Iron in Melt 0-3. Note the Numerous Fine Oxide Globules Near the Boundary of Oxide and Electrolytic Iron (Upper Boundary). $\times 100$ Fig. 12—Melt 0-3. Islands of Iron in Iron Oxide. $\times 100$.

too small (less than 0.005 millimeter in maximum diameter) to permit any tests except etching tests to be performed. They were found to survive as long as the oxide, in which they were embedded, survived. No definite conclusions about their nature could be made on the basis of this evidence alone. Examination of a large number of such crystals suggested, however, definitely their octahedral symmetry, and this combined with their color, association and resistance to reagents, led the author to believe that he was dealing with inclusions of magnetite, the existence of which had not been known heretofore.

The association of these inclusions with ferrous oxide is natural. Indeed, as was shown by Chaudron (13) and Eastman (29) ferrous oxide prepared at high temperatures becomes unstable on cooling and decomposes, in part, according to the reaction:



Some Fe_3O_4 is soluble in FeO as was shown by Matsubara (42); but if there be an excess over this amount it should crystallize out, provided opportunity for such crystallization is given. Apparently such opportunity is not given in the ordinary case of ferrous oxide inclusions, or else the solubility limits of Fe_3O_4 are not exceeded, because no traces of these "magnetite" crystals could be found in the artificially prepared FeO inclusions.

The possibility of the crystals being a compound other than Fe_3O_4 , a complex compound, perhaps made up of elements other than iron and oxygen, must, of course, also be kept in mind.

The melt O-3 was made in order to gain further insight into this matter. To obtain larger areas of ferrous oxide for metallographic testing, a crucible was machined from ingot iron, charged with pieces of electrolytic iron and a considerable amount of Fe_2O_3 , and heated to 1400 degrees Cent. in vacuo.

Fig. 10 shows a section near the bottom of the crucible which was chosen for examination. The diagonally reposing piece is electrolytic iron and the gray material, in the corner, between this piece and the walls of the crucible, the oxide.

The interpenetration of the oxide and the iron is shown by Figs. 11, 12 and 13. Of especial interest are the rounded oxide inclusions which have formed in the electrolytic iron in an area adjoining the oxide mass (upper portion of Fig. 11, right portion of Fig. 12).

Is FeO Dissolved by Iron at 1200-1400° Cent.?—Their existence would tend to imply that FeO was actually dissolved by the iron at 2550 degrees Fahr. (1400 degrees Cent.) and precipitated from it, on cooling, in the form of these rounded particles. Similar observations were made by A. McCance (37) who heated mild steel in contact with crushed mill scale at 2190 degrees Fahr. (1200 degrees Cent.), for 8 to 12 hours. Whiteley (37), in discussing McCance's paper, states that he also obtained interpenetration of iron and its oxide on long heating at elevated temperatures; he attributes this, however, to a penetration along grain boundaries rather than the solubility of the oxide in iron.

Just why the oxide should migrate along grain boundaries is not obvious—unless, indeed, these boundaries are small cracks—; it is equally obscure why the oxide penetrating along such “cracks” should deposit in the form of tiny spheroids rather than in the form of a continuous mass such as is actually observed in the oxidized cracks of annealed material. On the other hand, it is not easy to agree that FeO, at 2190 degrees Fahr. (1200 degrees Cent.), is soluble in solid iron to the extent suggested by the rounded oxides.

Are we not dealing here with a chemical reaction, taking place between solid substances, rather than solubility? Is not the formation of the small oxide islands but a preliminary stage of complete oxidation, such as is pictured in Fig. 12, where only few microscopic islands of iron have remained intact? Oxidation by solid oxide is effected, without doubt, through the medium of “solubility of the oxide in the metal,” but the size of the resulting islands of oxide is no more a measure of this solubility than the ratio of oxide to metal in Fig. 13.

What Causes the Formation of “Magnetite” Inclusions? The entire line of contact between the electrolytic iron and the oxide was searched for magnetite-bearing inclusions, but in vain. A number of them were found, however, on the line between the ingot iron and the oxide. Fig. 15 illustrates such an inclusion. Its size definitely assures us that it was not present originally in the ingot iron, and its formation in the ingot iron region implies the existence in ingot iron of something that is absent in electrolytic iron and that is essential for the formation of this type of inclusion. What could this something be? It happens to be the 0.02

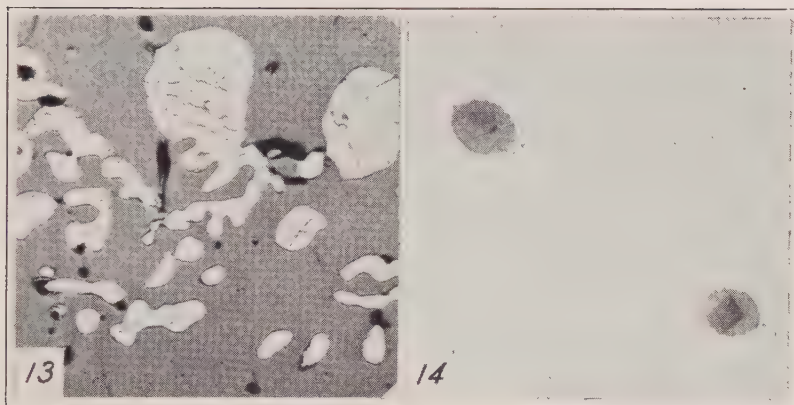


Fig. 13—Melt 0-3. The Oxide and Islands of Iron After Etching for $1\frac{1}{2}$ Minutes with 10 per cent HNO_3 . $\times 100$. Fig. 14—Ingot Iron. Oxide Inclusions with Crystals. $\times 1250$.

per cent sulphur, as will be shown in the chapter on oxide-sulphide inclusions (Chapter IV). Just how the sulphur accomplishes the release from the FeO of the hypothetical magnetite is not quite clear. It appears, however, that iron sulphide is soluble to some extent in iron oxide, and that, in the presence of dissolved sulphide, magnetite is not retained by FeO .

4. Manganese Oxide Inclusions

Melt O-4 was next made when attention was devoted to manganese oxide inclusions. Chemically pure Mn_2O_3 was charged in the electrolytic container and melted in air in order to avoid any loss of oxide, and additional Mn_2O_3 was dropped in the form of pellets on the molten metal which absorbed them readily. It was expected that the excess oxygen of Mn_2O_3 would oxidize some of the iron according to the equation:



Some FeO inclusions would then result alongside of inclusions of MnO (provided such inclusions exist) and opportunity would be had to examine the two oxides side by side and to compare their characteristics and properties.

Fig. 17 gives a general view of the inclusions which were found to have developed and which were observed to be more or less uniformly distributed throughout the ingot. These inclusions re-

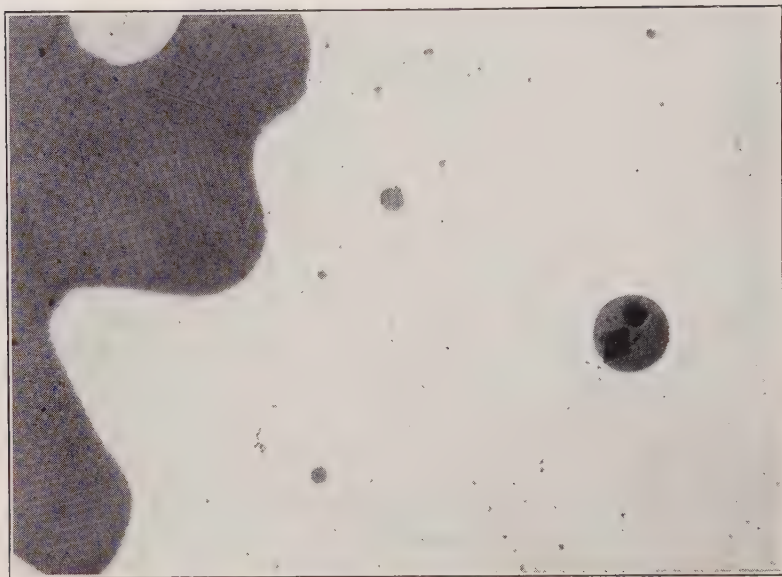


Fig. 15—Melt 0-3. An Artificial Crystal Bearing Oxide Inclusion Developed in Ingot Iron. $\times 500$.

semble very closely iron oxide inclusions, but appear to the trained eye a shade darker.

Fig. 18 is representative of the appearance of the inclusions at $\times 500$. They all look alike and appear to be homogeneous throughout. Are some of them FeO and some MnO ? Or are they all solid solutions of FeO and MnO ? Let us examine the experimental evidence.

Sulphur printing for 20 seconds had but little effect on pure iron oxide inclusions. In the present case all inclusions were dissolved by this treatment (compare Figs. 18 and 19). None of the inclusions are therefore iron oxide. We repolish the specimen, select another group of representative inclusions (Fig. 20) and proceed to apply the Campbell and Comstock method for their identification. Etching for 10 seconds with 10 per cent nitric acid induced some pits and irregularities to appear in the inclusions (Fig. 21) which, however, are not very serious. Chromic acid is without effect. Boiling sodium picrate slightly emphasizes the etching marks left by the nitric acid. 10 per cent boiling potassium

hydroxide induces no change (Fig. 22) ; finally, a saturated solution of stannous chloride disposes of all inclusions (Fig. 23).

According to Comstock, then, the inclusions are primarily iron oxide, and we just convinced ourselves, by the sulphur printing test, that they were not iron oxide. MnO , according to Comstock, should have been attacked by boiling sodium picrate. Yet, in the present case, the effect of this reagent was barely more pronounced than that of nitric acid.

The answer, of course, is that the inclusions are neither iron oxide nor manganese oxide but a solid solution or intimate mixture of the two.¹⁸ It will be seen later that ferrous oxide, although resistant to acids when pure, becomes susceptible to their attack when contaminated with sulphide. The presence of MnO (and, perhaps, of other oxides as well) seems to have an analogous effect. We were dealing, heretofore, with the inclusions en masse.

Applying high magnifications and searching patiently for evidences of heterogeneity, a number of inclusions were discovered (melt 0.4) portions of which exhibited a complex structure. It must be noted, however, that the proportion of the complex constituent in these inclusions was small in every case.

Figs. 24 and 25 illustrate the appearance of these inclusions at $\times 2500$. The main body of the inclusions consists of the uniform gray FeO-MnO solid solution, while at the rim a constituent of lighter gray (suggesting FeO) is seen, always accompanied by an almost equal proportion of a very dark material (most likely an oxide-rich in MnO).

In order to check the observations just made and, at the same time, to observe the effect of a greater relative proportion of iron oxide, another melt (0.5) was prepared with a mixture of equal parts of Mn_2O_3 and Fe_2O_3 as the inclusion material.

The resulting inclusions had exactly the same appearance as the inclusions of 0.4 and gave essentially the same reactions. The effects of the nitric acid and boiling sodium picrate etches were

¹⁸Another instance of apparently homogeneous FeO-MnO inclusions was observed when a pure iron-manganese alloy (8 per cent Mn) was annealed at a high temperature. Fig. 26 shows the appearance of the etched surface near a series of blowholes along which oxidation penetrated deeply. It is seen that the metal surrounding the holes is etched less deeply than the normal alloy. The depth of etch is a function of the manganese content and it is obvious that some manganese was removed from the metal near the holes, having been oxidized in preference to iron. The alloy is "demanganized" near the holes, as it were, much in the same way as steel is decarburized. While CO is volatile however, MnO is not and so the medium gray oxide masses seen in some of the holes (from the others they were removed by careless polishing) must contain both the MnO and FeO . Yet they are perfectly uniform and exhibit no indications whatever of a duplex structure.

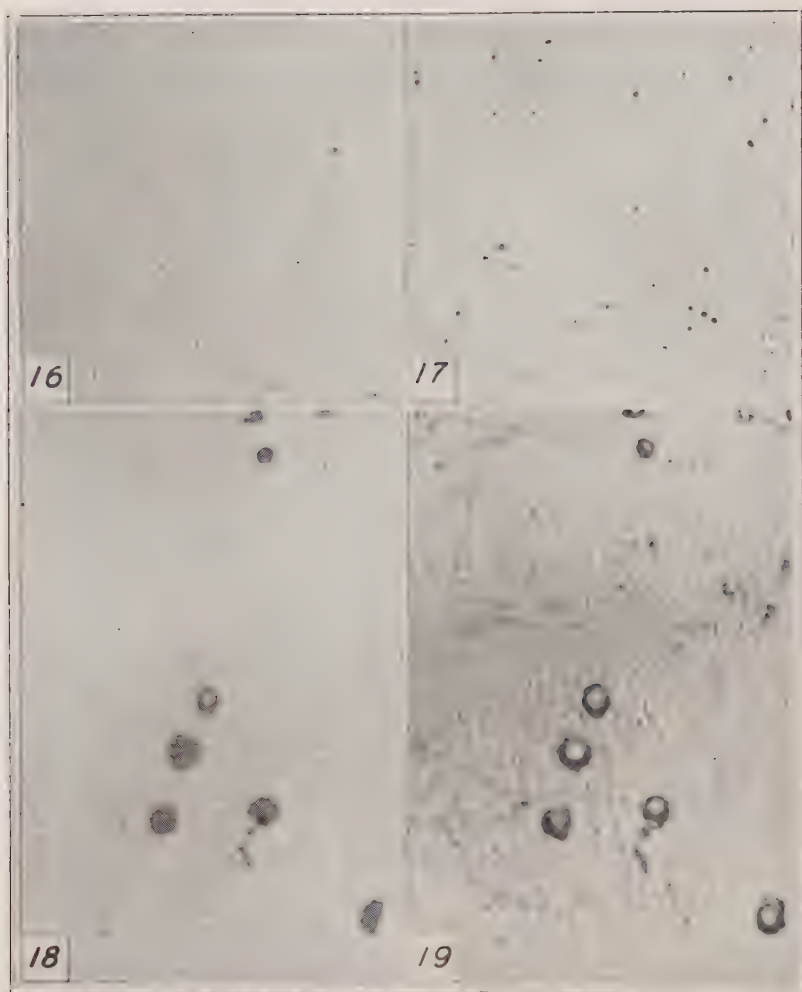


Fig. 16—Melt 0.2. Pure Iron Oxide Inclusions in Iron. $\times 100$. Fig. 17—Melt 0.4. Appearance of "Mixed" FeO-MnO Inclusions. $\times 100$. Fig. 18—Melt 0.4. A Group of "Mixed" FeO-MnO Inclusions at $\times 500$. Fig. 19—Melt 0.4. Same as Fig. 18 After Etching by 20 Seconds Sulphur Printing. All Inclusions are Destroyed. $\times 500$.

much less pronounced, however, showing that the resisting power of FeO-MnO inclusions increased with the decrease in relative MnO content.

The readiness with which manganese, in the presence of oxygen, leaves the metal bath is brought out by a comparison of the

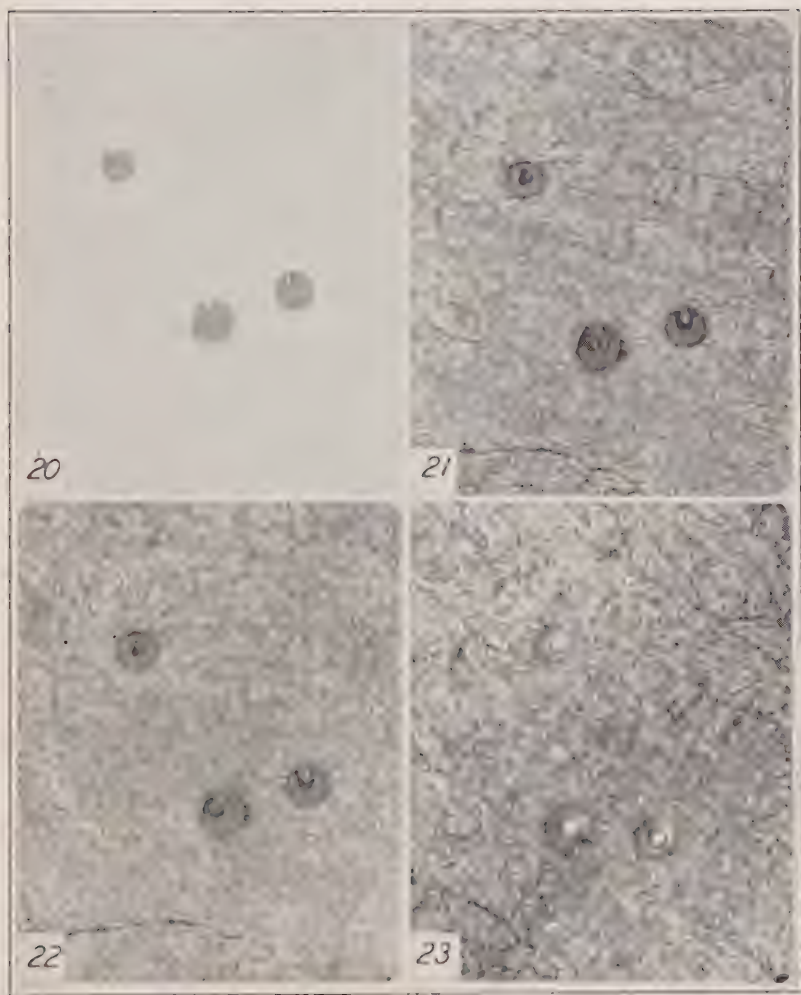
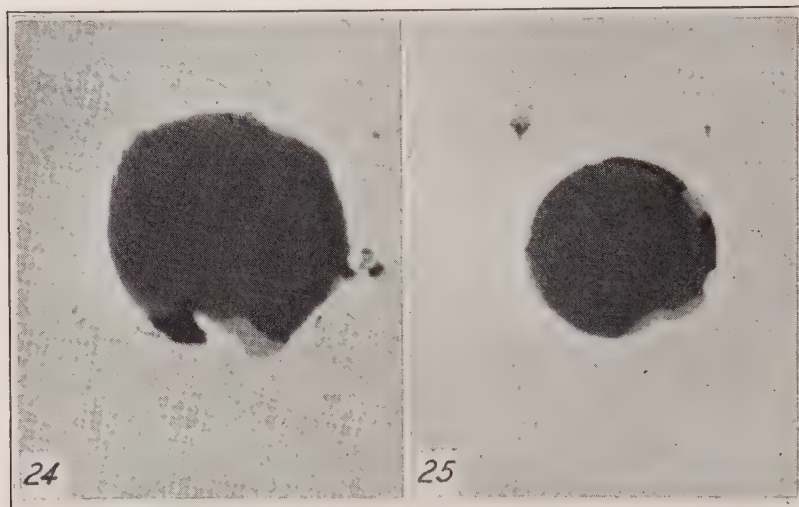


Fig. 20—Melt 0-4. A Selected Spot. $\times 500$. Fig. 21—Same as Fig. 20 After 10 Seconds Etching with 10 Per Cent HNO_3 . $\times 500$. Fig. 22—Same After 10 Minutes Etching with Boiling 10 Per Cent KOH . $\times 500$. Fig. 23—Same After Etching 10 Minutes with a Saturated Solution of Stannous Chloride in Alcohol. $\times 500$.

percentage found by analysis and the percentage charged, 4.85 per cent manganese was delivered into the melt 0-4, and only 0.3 per cent manganese was found to be present in the ingot. Out of 2.14 per cent manganese charged into melt 0-5 only 0.087 per cent manganese was preserved. Yet no manganese-rich oxide layer had



Figs. 24 and 25—Complex Inclusions in Melt 0-4. Note the Roughly Equal Proportion of Light and Dark Constituent Appearing at the Rim of the Inclusions. $\times 2500$.

formed on the top of the melt in either case. The walls of the crucibles were, however, discolored suggesting that the oxide had been absorbed by the relatively porous alundum.

The Constitution of "Manganese Oxide" Inclusions. From the observations just made it appears that MnO as such does not exist as separate inclusions in iron, barring individual, quite exceptional, or accidental inclusions. The question arises whether we had good reason to expect such inclusions to exist. The reaction



is known to be reversible; it is equally well-known that manganese is incapable of "deoxidizing" iron completely "no matter how much manganese is added" (McCance, 37). Any manganese added to molten iron distributes itself between the iron and the oxide in a manner governed by the concentration of the factors involved, and the temperature. That some manganese was actually reduced and passed into the iron, in the case of the melt 0-4, could be inferred from the relative readiness with which this metal was discolored on etching. The presence of MnO, then, necessarily implies the presence of FeO. The reverse is, of course, also true; i. e., if manganese be present in iron, the existence of FeO in the metal will imply the presence in it of MnO. Analyses of "oxide

inclusions'' made by a number of investigators substantiate this deduction.

Analyses of Oxide Inclusions¹⁹

| FeO | MnO | Observer |
|------|------|----------|
| 24.7 | 66.0 | Ruhfus |
| 23.1 | 71.0 | Ruhfus |
| 26.1 | 64.0 | Goerens |
| 20.4 | 63.1 | Hibbard |
| 28.3 | 66.2 | McCance |

The next question is: how will these two oxides react with each other? They are similar in their chemical characteristics, possess the same crystal symmetry (cubic) and crystal structure (NaCl type). It is difficult to see how they could avoid being soluble in each other, at least to a limited extent.

Photomicrographic evidence obtained by the writer points toward the existence of such solutions between FeO and MnO. Nor is this the only evidence. M. Matveieff, in 1910, (43) prepared "manganese oxide" inclusions by forging a wrought iron tube charged with Mn_3O_4 and heated to 2370 degrees Fahr. (1300 degrees Cent.). Matveieff's inclusions having never been in molten iron are not representative of true inclusions, to be sure; his observations, nevertheless, are of great value. Matveieff found the oxide to have agglomerated to a gray homogeneous mass interrupted by a network of a black constituent. The gray material gave indications of the presence of manganese, but was reduced by hydrogen, and was interpreted to be a solid solution of the oxides, rich in FeO. The black constituent was unaffected by hydrogen and was thought to be a solution rich in MnO.

In a later paper on similarly prepared inclusions (43), Matveieff revised his former descriptions and referred to the "black" constituent as a "brown" solid solution rich in MnO, and to the gray constituent as a eutectic between pure FeO and this "brown" solid solution.

The exact constitution of the FeO-MnO inclusions will be known definitely only when the equilibrium diagram of the system FeO-MnO is worked out. For the present it must be borne in mind that the existence of solid solutions between FeO and MnO

¹⁹Collected by McCance.

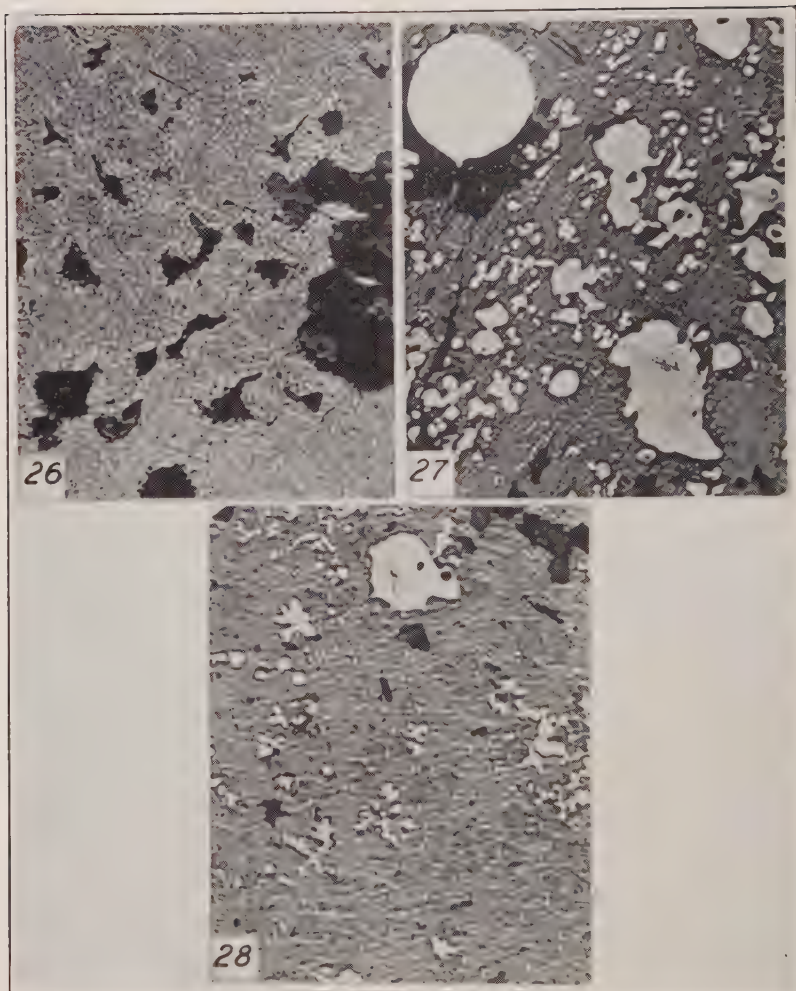


Fig. 26—Alloy of Pure Iron and Manganese (Manganese 8 Per Cent). Annealed and Etched with Dilute Nitric Acid. Note the Development of Uniform Gray Oxide and the "Demanganization" Around the Blow Holes. $\times 100$. Fig. 27—Ingot Iron Ladle Slag. Ferrous Oxide and Complex Silicates. Note the Iron Globule. $\times 100$. Fig. 28—Ingot Iron Ladle Slag. Another Spot. $\times 100$.

is clearly indicated, and that the occurrence of pure MnO inclusions is unlikely.

5. Alumina Inclusions

Before leaving the discussion of oxide inclusions a brief reference to alumina and silicate inclusions will be made although no

direct experiments concerning these inclusions were undertaken.

Description. Alumina inclusions were obtained by the writer when he prepared an artificial "ingot iron" (melting rusty sulphur-bearing electrolytic iron in an electric crucible furnace) and attempted to deoxidize the melt, just before pouring, with aluminum. On polishing the longitudinal section of rod forged from this material, elongated streaks of a hard substance were seen to be brought out in relief on the polished surface. Fig. 29 shows the appearance of these streaks at $\times 100$. It corresponds in all details to the excellent description of alumina inclusions given by F. Comstock (48).

The streaks consist of an aggregate of hard, blackish particles which are slightly rounded in outline. They have not been elongated by forging. The hardness of alumina causes the inclusions to stand out in relief, after preliminary polishing; and unless great care is exercised, they are easily dragged out of the section in subsequent polishing operations. The infusibility of alumina accounts (as was pointed out already by Comstock) for the small size of the particles and their failure to coalesce; and both the hardness and infusibility explain why alumina does not elongate on rolling.

An explanation for the elongation and segregation of a group of alumina inclusions into streaks has not been given, as far as the author is aware; this phenomenon is, however, merely an illustration of the behavior, on deformation, of any aggregate consisting of small, hard particles dispersed through a plastic matrix.

Fig. 30 shows a portion of the streak at $\times 2500$. The irregularity of the alumina particles is worthy of note. This irregularity in outline is further illustrated by Figs. 31 and 32, which show complex inclusions of alumina, iron oxide, and a sulphide-oxide eutectic. Such inclusions were formed where the amount of aluminum was insufficient to take care of all the oxygen.

Fig. 31 is illustrative of the case of only a slight deficiency in aluminum. The main dark portion of the inclusion is either alumina or iron aluminate; the small light gray protuberance in the right lower portion is FeO which is associated with a still lighter constituent, (indicated by the arrow), the FeO-FeS eutectic.

Fig. 32 shows no free iron oxide. In this inclusion a dark

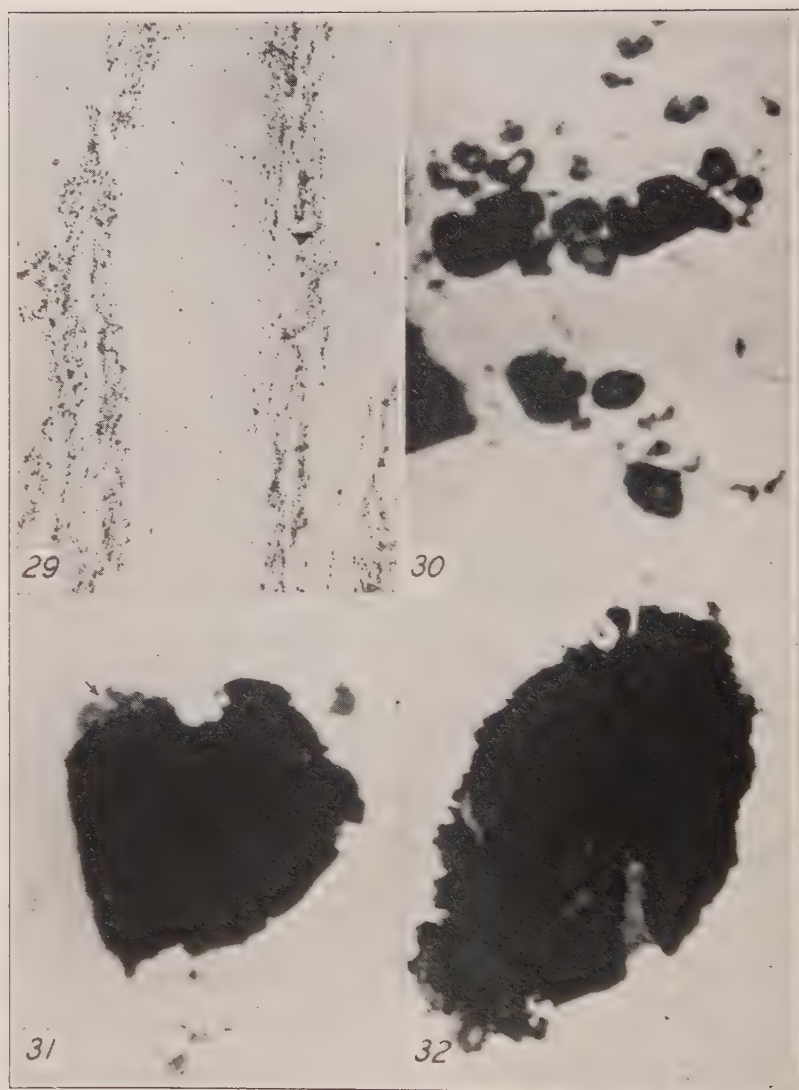


Fig. 29—Typical Streaks in an Iron Melt De-aired with Aluminum. $\times 100$. Fig. 30—Portion of the Streaks of Fig. 29. $\times 2500$. Fig. 31—A complex inclusion. The Main Part of it is Aluminum or an Aluminum Alloy. The Lighter Gray Layer Left Behind is FeO Associated with Some FeS. $\times 2500$. Fig. 32—Another complex Al_2O_3 -FeO-FeS inclusion. Note the Dark Gray Center Part, the Black Rim on the Right and the FeO-FeS Encrusted in a Crevasse, and at the Lower Rim. Note Also the Irregularity in Details of the Outline of this Inclusion. $\times 2500$.

compound intermediate in color between alumina and iron oxide is predominant; perhaps iron aluminate (or a solid solution of FeO in iron aluminate, for all we know); this is bounded by a darker rim suggestive of greater alumina content; finally the FeO-FeS eutectic is seen to be lodged in cavities on both sides of the inclusion, and in the form of a narrow envelop at the bottom.

Complexity of Oxide Inclusions. These photomicrographs are submitted as evidence of the complexity of oxide inclusions, even in so extreme a case as that of alumina whose high heat of formation, infusibility, chemical inertness and insolubility in iron would appear to guarantee its immunity from contamination.

We may safely conclude, in the absence of experimental evidence to the contrary, that pure FeO inclusions can form only in pure iron or in pure iron-carbon alloys. In the presence of other elements, introduced intentionally or present as impurities, iron oxide will always be contaminated by the oxides of these elements. Thus an oxide inclusion in an iron-manganese-nickel alloy, for example, will be a complex (solid solution or aggregate of solid solutions) of iron, manganese and nickel oxides whose relative proportions will be governed by the equilibrium relations existing in the metal bath, in the neighborhood of the inclusion, at the instant of its formation.

This applies, of course, not only to the oxides. It will be seen, in the chapter on oxide-sulphide inclusions, that sulphides, in the presence of oxides, will invariably be associated with the oxides, and even dissolve in them to a limited extent.

The oxide of silicon is no exception either—it merely happens that we are accustomed to designate complexes of the more basic oxides with silica as silicates rather than as complex oxides.

6. Silicates in Iron

Sources and Formation. Silicates are formed on the interaction of basic oxides, such as FeO and MnO , with the oxide of silicon, SiO_2 , as is well known. Silicon as such is introduced into steel through the pig iron, and is oxidized to SiO_2 by the same agencies that yield the basic oxides, i. e., the iron ore and the oxidizing blast or furnace gases. In addition, silica and silicates are present in the furnace walls, ladle lining, etc. The slag formed in steel making consists essentially of silicates.

Silicate inclusions, broadly speaking, can originate in three distinct ways, namely, from

- (1) Mechanically entrapped fragments of the brickwork and lining
- (2) Mechanically entrapped slag particles
- (3) Reaction products of the bath.

In the author's opinion the first two possibilities have been largely over-emphasized. There is little opportunity given for the slag from the blanket to become entangled in liquid iron; it is equally unlikely that fragments of the brickwork should disperse themselves in a more or less uniform manner through the metal bath. Such silicate inclusions as are found in iron and steel, (barring exceptional inclusions), must have originated in a manner quite analogous to that of other oxide inclusions.

The formation of silicate inclusions as reaction products does not necessarily imply any marked solubility of silicates in molten iron, although contrary to accepted notions, a slight solubility is indicated. As pointed out by McCance (37), who holds silicates to be insoluble in iron, the formation of silicate inclusions can be depicted as follows:

- (1) The FeO of the slag oxidizes the carbon of the bath and eliminates itself thereby gradually
- (2) As the concentration of FeO in the slag falls SiO_2 begins to oxidize the carbon, metallic silicon being formed which passes into the bath
- (3) The slag becomes viscous and, to restore its fluidity ore is added which increases the concentration of FeO which, in turn, resumes its oxidizing functions. This causes a re-oxidation of the silicon in the bath resulting in the precipitation of the insoluble silica "as a cloud of minute inclusions throughout the bath"
- (4) "Any silicate particles so produced will be attacked by metallic manganese to form manganese silicate."

This description depicts, probably, quite correctly the formation of many silicate inclusions. It is equally probable, however, that it does not tell the whole story.

Solubility of Silicates in Molten Iron. In particular, the generally accepted view of the complete insolubility of silicates in molten iron is open to doubt. In order to gain some information

on this point and, at the same time, to see whether "a cloud of minute inclusions" will form throughout the metal bath in the absence of the mechanism given by McCance, two melts of the electrolytic iron and of silicates of iron and manganese (C. P.) were prepared in the usual way (melts 0-6 and 0-7). The resulting ingots were both found to contain tiny rounded inclusions not unlike those of the oxide melts; the inclusions, here, appearing merely much darker. Now, the melting points of the various manganese silicates are in the neighborhood of 2370 degrees Fahr. (1300 degrees Cent.), and those of the iron silicates (with the exception of Gruenerite, perhaps) are also below the melting point of iron. Ample opportunity was given for the silicates to agglomerate and to fuse in the electrolytic container before the collapse of the latter. If completely immiscible with, and insoluble in the iron, the agglomerated silicates would then be expected to float bodily to the top of the melt upon fusion of the container. Instead they were found to be dispersed throughout the melt as tiny rounded particles.

Must we not conclude that molten iron, at high temperatures, is capable of dissolving, partly, some silicates? Or at least, that molten iron is capable of being "silicized" in the same manner as solid iron is capable of being oxidized at elevated temperatures. It is difficult, of course, to draw definite conclusions on the basis of one or two experiments; the results, nevertheless, are worthy of consideration.

The chemical analyses of the melts do not give reliable information, unfortunately. Silicates are practically insoluble in the reagents employed for analysis; they may, nevertheless have been attacked partly, and may have furnished thereby the 0.056 per cent silicon which was found in the melt 0-6 and the 0.02 per cent silicon and 0.05 per cent manganese found in 0-7. But it is not unlikely that a portion at least of the manganese and of the silicon found was present in the iron in the metallic state, the molten iron actually having reduced the silicon and the manganese from the silicate.

It will be safe to admit that the fundamental factors of concentration and of temperature are just as important in determining the course of silicate-metal reactions as the course of any other reactions. And that, therefore, in the case of silicates, just like

in the case of oxides, inclusions will form, the composition of which is governed by the concentration of the elements present and the temperature.

We must not forget, of course, that the composition of the metal bath is a function of the composition of the slag and that, with changes in the slag, changes in the metal phase will also take place. These changes, in many instances, may cause the formation of suspended inclusion droplets already in the molten iron. This applies to the case of oxide inclusions in general.

Constitution of Silicate Inclusions. Having gained some insight into the process of formation of silicate inclusions, the next question that presents itself is whether we are justified in drawing a rigid line of demarcation between iron silicate and manganese silicate inclusions, such as is drawn, for example, in Campbell and Comstock's "Method for Identification." We found that there was no basis for such a division in the case of simple oxides. It is fairly evident that there is still less justification for such a division in the case of silicates which are known to occur naturally in a variety of forms in which MnO replaces FeO isomorphously.

Let us examine, however, the experimental evidence. Fig. 33 shows two representative inclusions of the melt 0-7. They appear homogeneous despite the presence in them of both iron and manganese silicates. Nitric and chromic acids are without effect on these inclusions. Sulphur printing for 20 seconds induces no changes. Boiling sodium picrate attacks the majority of the inclusions although it fails to eliminate them (Fig. 34). Does this indicate the presence of MnO? Possibly. We next etch with 10 per cent boiling potassium hydroxide. No changes are indicated (Fig. 35). Hence there are no manganese silicates present, according to Comstock. Stannous chloride is also without effect, while hydrofluoric acid completely dissolves the inclusions (Fig. 36) which are thus identified as iron silicate (?). We do not know what the exact composition of the inclusions is. We can be certain, however, that they are complex iron-manganese silicates. Pure manganese silicate inclusions do, probably, occur but very rarely in pure iron for the same reasons that make the presence of pure MnO inclusions unlikely.

In general, it can be said that, in the presence in iron of manganese, silicon and oxygen, iron-manganese silicates will form,

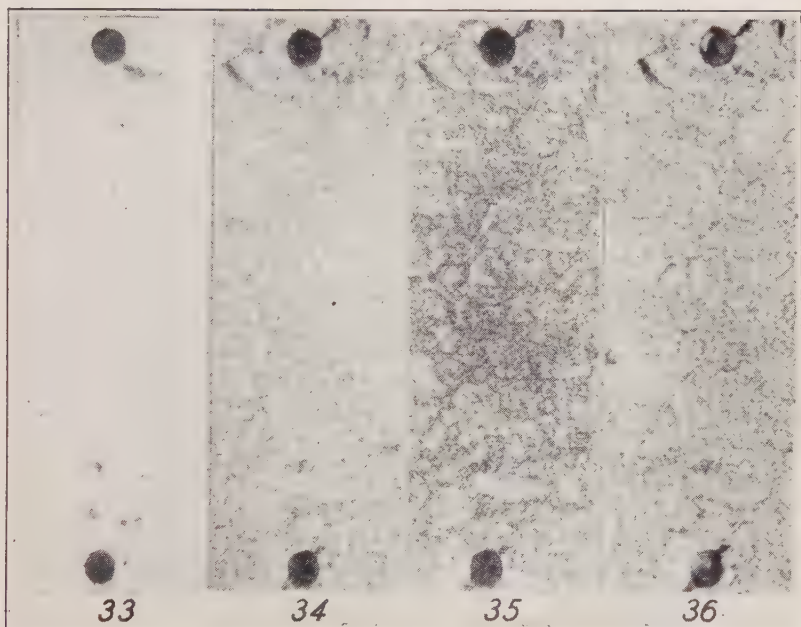


Fig. 33—Melt O-7. Two Representative Inclusions. $\times 100$. Fig. 34—Same After Etching for 10 Minutes with Boiling Sodium Picrate. $\times 100$. Fig. 35—Same as Fig. 34 After Etching for 10 Minutes with Boiling 10 Per Cent KOH. $\times 100$. Fig. 36—Same After Etching for 10 Minutes with a 20 Per Cent Aqueous Solution of Hydrofluoric Acid. $\times 100$.

associated with such excess oxides as are present. These silicates and oxides will form partial solid solutions, eutectics, etc., and among themselves and among each other, the exact constitution of the inclusions being governed, in each individual case, by the fundamental factors of concentration and temperature, applying to this case.

Photomicrographs of Silicate-Oxide Aggregates. Fig. 28 is a picture at $\times 100$ of ingot iron ladle slag. The brilliant white islands appear, at first sight, to be included blobs of iron. This is, however, merely an illusion. We judge color and more especially brilliancy solely by contrast. In the presence of metallic iron the oxide of iron appears quite dull and gray, in the presence of a dark silicate it appears as brilliant and white as iron. The whitish islands are iron oxide. This becomes clear when we inspect Fig. 27, which shows the appearance of a real inclusion of metallic iron. The silicate groundmass appears, (in both pictures,) mottled, indicating the presence of several constituents. Higher magni-

fications reveal that the mottled appearance is due to the presence of a fine silicate-oxide eutectic (Fig. 37). The main mass of the silicate is fairly homogeneous in spite of the complexity of its composition.

Let us now consider another case, the case of some perfectly formed skeleton crystals of fayalite which were found in the brickwork of an open-hearth furnace. Fig. 38 serves to describe these crystals.

Perfection of crystal symmetry is no longer held to be a criterion of the purity of a mineral; one, nevertheless, would expect a perfect crystal to be less heterogeneous than a complex slag. The microstructure of the specimens tells another story. The differences in shade observed in the regular plates of Fig. 39 are unquestionably ascribable to a difference in orientation alone. Individual patches of a darker gray constituent different from the main mass, are however, observed here and there. Different eutectics which were found to be present in the specimen are illustrated by Figs. 40 and 41. Finally Fig. 42 shows a string of included typical magnetites.

We can learn from these observations that complex silicates can be homogeneous as well as heterogeneous, that they dissolve a considerable amount of iron oxide which may separate as a constituent of an eutectic or eutectoid; that, further, eutectics or eutectoids form among the silicates themselves, and that different classes of silicates form partial solid solutions among each other.

7. Summary

On the basis of fundamental physico-chemical data, the experiments of earlier investigators and the observations of the author the following conclusions can be drawn about oxide inclusions:

I. Sources. Oxides will invariably form in the presence of oxygen; the source of oxygen, in the Bessemer process, is the air blast, in open-hearth practice, the iron ore and furnace gases. The complex oxides known as silicates are also introduced from the brickwork of the furnace, the ladle lining, etc.

II. Formation. Iron oxide is soluble in molten iron and will be precipitated on solidification, in the form of oxide inclusions which will be the more numerous the higher the original oxygen content of the bath and the lower the carbon.

In the presence of manganese, or of any other oxide forming



Fig. 37—Ingot Iron Ladle Slag. Ferrous Oxide in a Matrix of Complex Silicate and Silicate-Oxide Eutectic. $\times 2500$.

metals soluble in iron, oxides of these metals will form at the expense of iron oxide, to an extent governed by the equilibrium conditions existing in the metal bath.

If an oxide thus formed is largely insoluble in the molten metal and opportunity is given for it to leave the bath, true "deoxidation" of the bath is effected. Deoxidation by ferro-

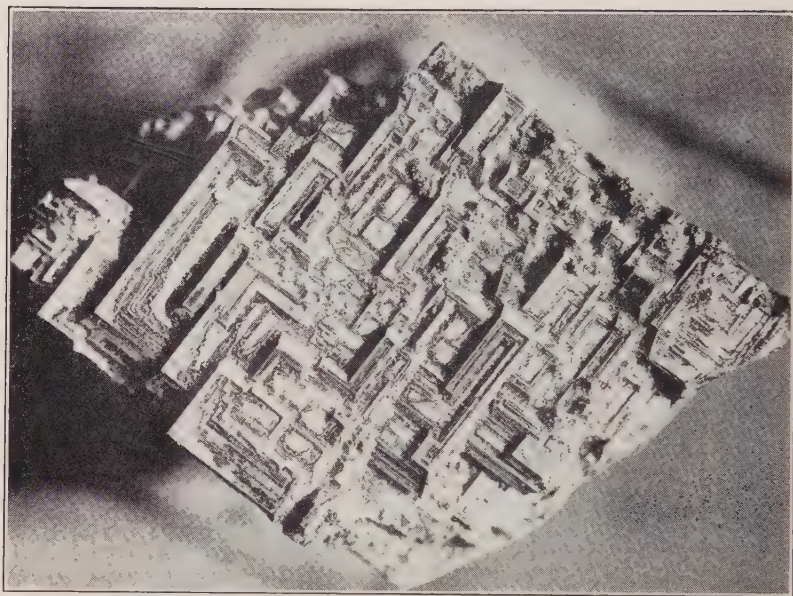


Fig. 38—General View of the Fayalite Crystals. $\times 3\frac{1}{2}$.

manganese is limited since manganese oxide is somewhat soluble in iron. Deoxidation by ferrosilicon is more complete since silica and silicates are soluble to a very small extent in iron.

Oxide (and silicate) inclusions form not only due to the precipitation of dissolved oxides at the instant of solidification of the metal, but also due to precipitation prior to solidification, whenever the changing composition of the metal and slag systems induces such precipitation.

III. Constitution. Pure iron oxide inclusions, at atmospheric temperature, consist of a solid solution of Fe_3O_4 in FeO . In the presence of sulphides (in solid solution in FeO) Fe_3O_4 may be liberated in the form of magnetite crystals (?).

If manganese be present, the oxide inclusions will consist of a solid solution of iron and manganese oxide, or of an aggregate of such solid solutions, the constitution of each individual inclusion being a function of the equilibrium conditions prevailing in the metal bath, in the neighborhood of the inclusion, at the time of its formation. Pure MnO inclusions can occur only as individual, quite exceptional, inclusions in iron and steel.

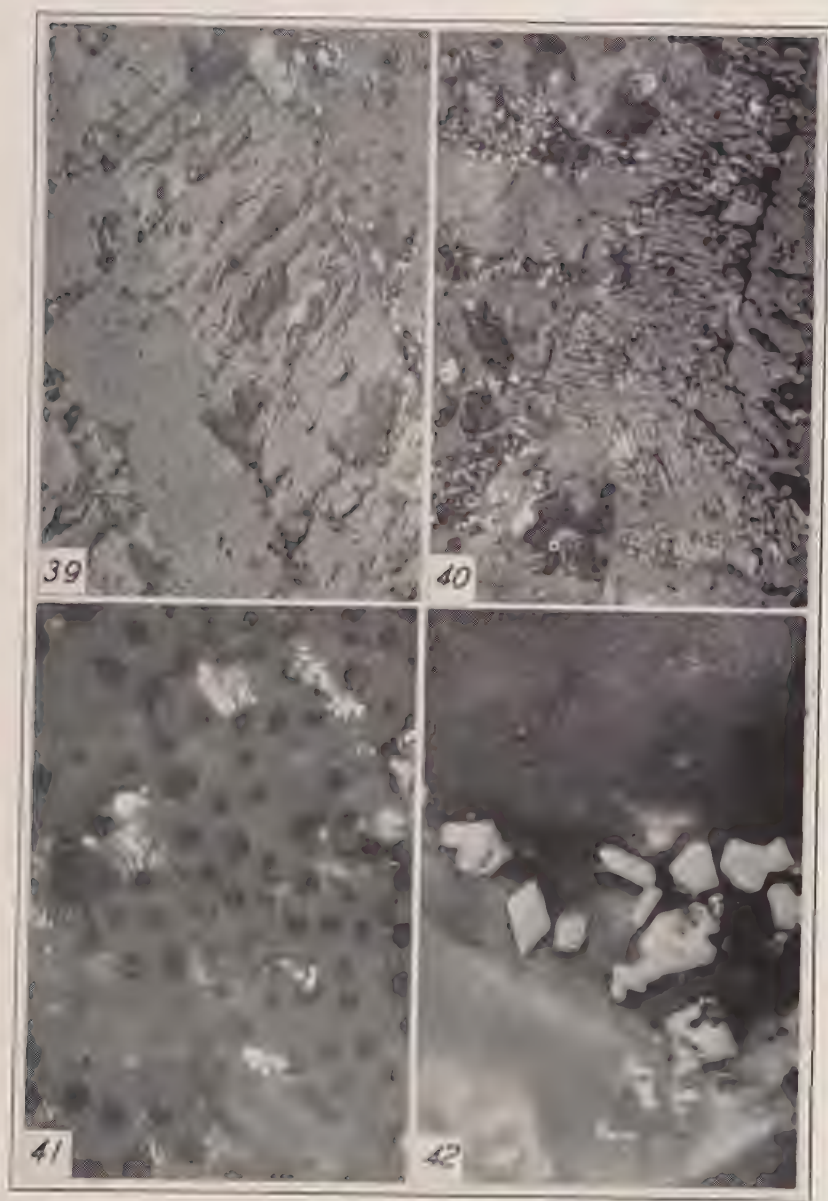


Fig. 39—Fayalite Crystals. Bands of Twinned (?) Plates. Note the Presence of a Dark Gray Constituent and of Numerous Bright Spots. The Latter are Magnetite Crystals. $\times 500$.
Fig. 40—A Eutectic Within the Crystal. $\times 500$. Fig. 41—Another Eutectic. $\times 2500$.
Fig. 42—Magnetite Crystals Within the Fayalite Crystal. $\times 2500$.

In general, in the presence of foreign elements, oxides of these elements will be associated with iron oxide in a manner depending on the chemical relationship existing between them and iron oxide. In particular, in the presence of silicon, silicates will form, and free simple oxides are exceptional. It is unlikely that pure manganese silicate exists in iron and steel.

IV. Behavior. No evidence has been advanced which would show conclusively that oxide inclusions "migrate" in the metal after solidification. In the absence of such evidence it is postulated that oxide inclusions, under ordinary circumstances, remain where they were born.

Working at high temperatures (above 1100 degrees Cent.) elongates pure or relatively pure iron oxide inclusions; particles measuring below 0.005 millimeters in diameter are, generally, not elongated. The same applies to silicate inclusions which, however, appear to be elongated more easily than the oxides.

Little is known about the rolling characteristics of other complex oxides. Alumina is not elongated on hot working; it is however thrown into elongated streaks.

V. Appearance. Pure iron oxide inclusions are of a medium gray color and appear, in the cast metal, as small rounded particles (maximum diameter generally below 0.01 millimeter).

Iron-manganese oxide inclusions are similar to those of pure iron oxide, exhibiting, however, a darker shade of gray.

Silicates are distinctly gray or greenish-black and have a glossy, or greasy, appearance.

Magnetite inclusions are of a dark gray color and exhibit geometric forms suggestive of octahedral symmetry.

Alumina inclusions are almost black, exhibiting semi-angular, semi-rounded irregular forms, the detailed outlines of which are highly irregular. Their maximum diameter seldom exceeds 0.005 millimeters.

VI. Reactions. Pure iron oxide inclusions are very little affected by the action of 20 seconds sulphur printing, while MnO-bearing oxides are removed or pitted by this treatment. Sulphur printing has no effect on silicate inclusions.

Stannous chloride dissolves oxide inclusions, both in the absence and presence of MnO, and leaves silicates unchanged.

Boiling sodium picrate generally indicates the presence of

manganese oxide by lightly attacking the complex oxide. Its action is not decisive however.

Dilute hydrofluoric acid dissolves silicate inclusions.

APPENDIX TO CHAPTER II

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CHAPTER III

SULPHIDE INCLUSIONS

1. *Brief Review of Earlier Work*

THE first inclusions that were recognized in steel, and described in the literature were sulphides.

The detrimental influence of sulphur on the rolling properties of steels and the beneficial effect of manganese in correcting this were early recognized by steel makers and aroused early the curiosity of metallurgists (1, 2, 3). Osmond and Werth (4) were the first to show—in 1885—that the sulphur in steels containing manganese existed as the sulphide of manganese. They arrived at this conclusion from a chemical study of steel.

Microscopical study of failures of steel parts by Andrews²⁰ appears to have led to the first discovery of sulphide inclusions. The microscope then was applied to a study of the form in which these inclusions occur, by Arnold. He describes (11, 13), iron sulphide inclusions as of “pale brown color”, existing, first, as “globules” or “ovoids”, second, “as thin laminae of an irregular oval shape” and third, “as cell walls presenting in section a mesh-like appearance”; he classes the second form as “dangerous” and the third as “most dangerous”. Manganese sulphide, according to Arnold, appears as “dove-colored globules or ovals, sometimes as oval laminae, but . . . very rarely as meshes, manganese seeming to almost entirely prevent the formation of cell walls of sulphide.”

Le Chatelier, in 1902, in a brilliant paper on the “Sulphide of Iron” (16) broadly confirmed the observations of Arnold. He further noted the infusibility of MnS and the incompleteness of sulphur removal by manganese; described for the first time the sulphide-oxide eutectic and explained the difference in the distribution of FeS and MnS in the metal.

Some of Le Chatelier's observations were, in turn, confirmed by Arnold and Waterhouse (17).

The next important contribution to the knowledge of sulphide inclusions was furnished by Treitschke and Tammann (23)

²⁰“Microscopic Examination of Flaws Inducing Fractures in Steel.” 1896, p. 20.

who worked out the first equilibrium diagram of the system Fe-FeS. This diagram appears to be faulty in many important details, and has been misquoted and misinterpreted by later writers.

E. F. Law (25), in 1907, pointed out that the sulphide occurring in steels "varies very much in color and composition" and correctly surmised that this was ascribable to "manganese sulphide dissolving a certain amount of iron sulphide". Law disputes, however, Le Chatelier's statement about the high melting point of MnS. He states: "the author . . . had no difficulty in melting manganese sulphide in an ordinary coke-fired assay furnace, which was quite incapable of melting mild steel."

Some years later (1911) D. M. Levy (33) found that "pure manganese sulphide requires a temperature of upwards of 2640 degrees Fahr. (1450 degrees Cent.) in order to cause fusion." He also found that manganese and iron sulphides were soluble in all proportions when molten, and partially soluble (MnS holding a maximum of 50 per cent FeS in solid solution) when solid. He distinguished between three types of manganese sulphide:

- "(a) dark colored, more free from FeS and most infusible;
- (b) paler varieties, containing up to 50 per cent FeS in solid solution, more fusible;
- (c) composite sulphides consisting of MnS-FeS solid solution together with FeS itself."

The latter findings of Levy were, in substance, confirmed by the work of G. Röhl (37) which marks another important advance in our knowledge of sulphide inclusions. Röhl worked out the first FeS-MnS equilibrium diagram; he established the existence of solid solutions between FeS and MnS, and, as he thought, the existence of a compound $\text{Fe}_3\text{Mn}_2\text{S}_5$. He found the melting point of MnS to be in the neighborhood of 2950 degrees Fahr. (1620 degrees Cent.), verifying thus the original contention about the relative infusibility of MnS of Le Chatelier.

A. L. Field in discussion (46) disapproves of Röhl's ideas, stating: "It is not true that a solid solution of the two sulphides separates from iron on solidification." He finds that Röhl's FeS-MnS system "fails to check the data of Levy", also that "conclusions based on these erroneous results are employed in his later de-

ductions regarding occurrence of sulphides in the very small melts employed.”

A. McCance (41), referring to the evidence advanced by the work of Arnold and Bolsover (38), also disputes the correctness of Röhl's contentions in regard to the existence of solid solutions of MnS-FeS. Examining the “evidence” he finds that “no real support” for the conclusions of Röhl can be found. The reaction



is not a balanced one, according to McCance, and accordingly “sulphide inclusions in steel . . . may be MnS, but they are not likely to contain any FeS even in a state of solid solution.”

The existence of FeS-MnS solid solutions was, however, advocated again by Zen'ichi Shibata (48), who, recently, worked out a new FeS-MnS equilibrium diagram which differs from that of Röhl in many details. Shibata checks the melting point of MnS as determined by Röhl, giving it as 2930 degrees Fahr. (1610 ± 3 degrees Cent.)

The contention of McCance about the irreversibility of the reaction



was justified, according to A. L. Feild in discussion (47), since

“by far the greater weight of evidence inclines toward two conclusions:

- (1) That the reaction proceeded toward the right to practical completion in the ideal case of the three-component system Fe-Mn-S with iron in large excess; and
- (2) That the presence of oxygen as a fourth component was responsible for that apparent reversibility which occurs to so marked a degree in ordinary steel practice.”

A. L. Feild finds further that the paper of Herty and True (47) in which the latter attempt to prove the reversibility of the reaction “brings forward the first reliable evidence of a direct sort to support the view that the reaction is reversible.” He fails to see however, that Herty and True were dealing with oxy-sulphides,²¹ as

²¹The melts were apparently conducted in air.

shown by their Fig. 2, for example, and that therefore the presence of oxygen, again, can be blamed for the "apparent reversibility."

It should, perhaps, be mentioned, that Arnold and Bolsover (38), in 1914, recorded "the probable existence in fluid commercial steels of a eutectic of ferrite and sulphide of manganese which has a very high freezing point." This statement has been largely ignored by later investigators.

Individual important papers bearing directly on some of the questions that presented themselves in the course of the author's study will be discussed in greater detail in the appropriate connections later.

From the above brief review of outstanding papers on sulphide inclusions it is evident that agreement is lacking. In particular, the existence of solid solutions between MnS and FeS is doubted by many; widely divergent figures have been given for the melting point of MnS; the proof of the reversibility of the reaction $\text{FeS} + \text{Mn} = \text{MnS} + \text{Fe}$ is open to criticism. The question of a possible eutectic of ferrite and manganese sulphide must be considered. The exact manner in which the inclusions form has not been adequately explained; least of all the behavior, in the presence of MnS, of FeS which, according to McCance (41) for example, would, upon heating of steels to above 1795 degrees Fahr. (980 degrees Cent.), "redissolve and diffuse into the surrounding steel, and on cooling again . . . would not be re-deposited in its original position, but would be deposited in between the crystal grains according to its habit".

In the photomicrographic studies, about to be described, the writer endeavored to pay particular attention to these doubtful points.

3. Iron Sulphide and Iron

Five melts of electrolytic iron and pure sulphur were prepared for the study of the iron-iron sulphide relationships. The purity of the melts was checked by analyses which showed the presence of only traces (less than 0.001 per cent) of manganese and of some 0.009 per cent carbon.

Ingots containing from 0.016 per cent sulphur up to 1.05 per cent sulphur were obtained, a range which surely embraces the industrially important cases.

Table II
Experimental Melts

| Melt | Charge (grams) | To yield* Per Cent | Chemical Anal- yses of the melt Per Cent | Remarks |
|------|--|--|---|---|
| S-1 | El. Fe 51.35 S. 1.00 52.35 | S 1.78 (Fe S 4.9) | Mn Trace S 1.05 (Fe S 2.89) | Melted in vacuo. Loss of sulphur in this and the other melts is explained by the great tendency of sulphur to escape through the joints between cover and container—probably prior to absorption by iron. |
| S-2 | El. Fe 28.90 S .53 29.43 | S 1.8 (Fe S 4.95) | Not analysed; probably like S-1 | Solidified slowly (in the course of about 15 min.); cooled slowly. |
| S-3 | El. Fe 135.81 .45 136.26 | S 0.33 (Fe S 0.91) | Mn Trace C 0.009 S (Top) 0.135 (Fe S 0.344) S (Bottom) 0.100 (Fe S 0.275) | Solidified and cooled fairly rapidly. |
| S-4 | El. Fe 93.80 S 0.18 93.98 | S 0.19 (Fe S 0.52) | S 0.033 (Fe S 0.091) | Loose fitting cover. |
| S-5 | El. Fe 43.6 Melt S-4 43.7 87.3 | S 0.017 (Fe S 0.046) | S 0.016 (Fe S 0.045) | No sulphur escaped, since it was charged as an alloy with iron. |
| S-6 | El. Fe 80.37 Mn 1.10 S 1.30 82.77 | Mn 1.33 S 1.57 (Mn S 2.11) + Fe S 2.19) | Top fourth Mn 1.47 S 0.79 (Mn S 2.15) + Mn 0.11) Bottom fourth Mn 0.58 S 0.71 (Mn S 0.92) + Fe S 1.02) | Manganese metal charged into the middle of the container with sulphur above and below it. |
| S-7 | El. Fe 65.00 Mn 1.75 S 1.00 67.75 | Mn 2.58 S 1.48 (Mn S 4.02) + Mn 0.04) | (C 0.17) Mn. 1.53 S 0.63 (Mn S 1.71) + Mn 0.45) | As above. |
| S-8 | El. Fe 65.40 Mn 6.15 S .85 72.40 | Mn 8.5 S 1.17 (Mn S 3.17) + Mn 6.50) | Mn 6.42 S 0.40 (Mn S 1.10) + Mn 5.72) | Manganese charged on the bottom of the container and the sulphur on top of it. |

*Allowance was made in every case for the escape of sulphur during the melting in vacuo; hence these figures are not representative of what the melts were expected to analyze.

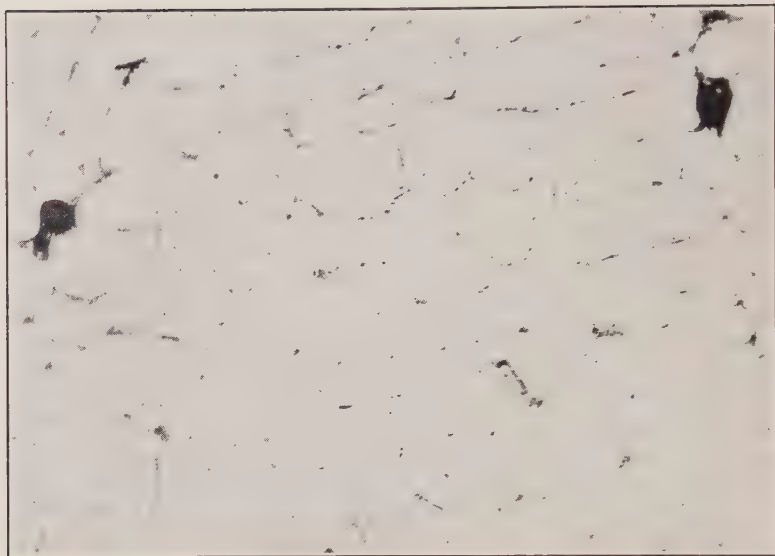


Fig. 43—Photomicrograph of Melt S-1 As Cast Showing the "Cell Wall" or "Enveloping Membrane" Structure of Iron Sulphide. $\times 100$.

THE HIGH SULPHUR MELTS

(S-1 and S-2)

Description of Inclusions. The high sulphur melt S-1 exhibited the well known "cell-wall" or "enveloping membrane" structure of iron sulphide, illustrated in Fig. 43. The continuity of the metallic mass is seen to be broken up completely,—and this is accomplished, in the present case, by but 1.05 per cent sulphur (2.9 per cent FeS).

Pure iron sulphide is decidedly yellow when contrasted with the brilliant white of the iron; it is, however, a very pale yellow, a "cream" yellow, perhaps. It appears homogeneous throughout, no trace of a eutectic or duplex structure being discernible at the highest magnifications.

High magnifications reveal that not all of the sulphide is concentrated in cell walls; the iron matrix itself is seen to be peppered with tiny rounded sulphide globules. (See Figs. 44 and 45). The larger of these globules seldom measure over 0.0015 millimeters in diameter while the smallest ones that could be identified were of the order of 0.0001 millimeter in diameter (0.1μ). The

globules are not always as pronounced as they happen to be in S-1, which, as records revealed, were allowed to solidify and cool rather rapidly. In the melt S-2 of the same composition as S-1, but solidified and cooled slowly, the metallic matrix was found to be much cleaner than in S-1. Small sulphides were not entirely absent, to be sure, but areas essentially free of them could be found with ease (See Fig. 46 and especially Fig. 47, and compare with Figs. 44 and 45, respectively).

Formation of the "Cell-Wall" Structure. Cell-walls are the "habit" of FeS, or FeS "segregates to the grain boundaries forming continuous envelopes around the crystalline grains of the metal" are statements not infrequently met with in the literature. Such statements are highly inaccurate and misleading as will be shown in a later connection (Chapter V); moreover, they do not explain anything.

The facts are simple. Iron sulphide is soluble in molten iron as was shown already by Treitschke and Tammann (23). As the iron solidifies, the sulphide, or at least a considerable proportion of the sulphide, is thrown out of solution and this sulphide being in a molten condition,²² is forced into the interstices between the iron dendrites where it finally solidifies.

The regularity of the cellular structure is suggestive of such a mechanism, although, failing to see the iron dendrites, it is not always easy for one to correlate the observed sulphide patterns with dendritic fillings. Areas like the ones depicted in the panoramic photomicrograph Fig. 48, show the relationships fairly clearly, yet even here the details exhibited are too pronounced to bring out the general aspects of these relationships. A macro-picture is called for—and this is furnished in an admirable manner by the well known method of sulphur printing invented by Heyn and Bauer (22) and modified by Baumann.²³ This method has been used by numerous investigators, reproductions of sulphur prints, for example, being given in the papers of Levy (35) and of Arnold and Bolsover (38); yet, to the author's knowledge, it has never been successfully applied to a study of the solidification relationships between iron and iron sulphide, to which it is so well adapted.

²²Melting point of pure FeS is 1193 ± 50 degrees Cent. according to the International Critical Tables.

²³*Revue de Metallurgie*, III, p. 416.



The Matrix of High Sulphur Iron. Fig. 44—Photomicrograph of Melt S-1. Tiny Rounded Sulphide Globules in Iron Matrix. $\times 500$. Fig. 45—Photomicrograph of Melt S-1. Part of Fig. 44. $\times 2500$. Fig. 46—Photomicrograph of Melt S-2. Note the Relative Cleanliness of the Matrix of this Slowly Cooled Melt. $\times 500$. Fig. 47—Photomicrograph of a Part of Fig. 46. $\times 2500$.

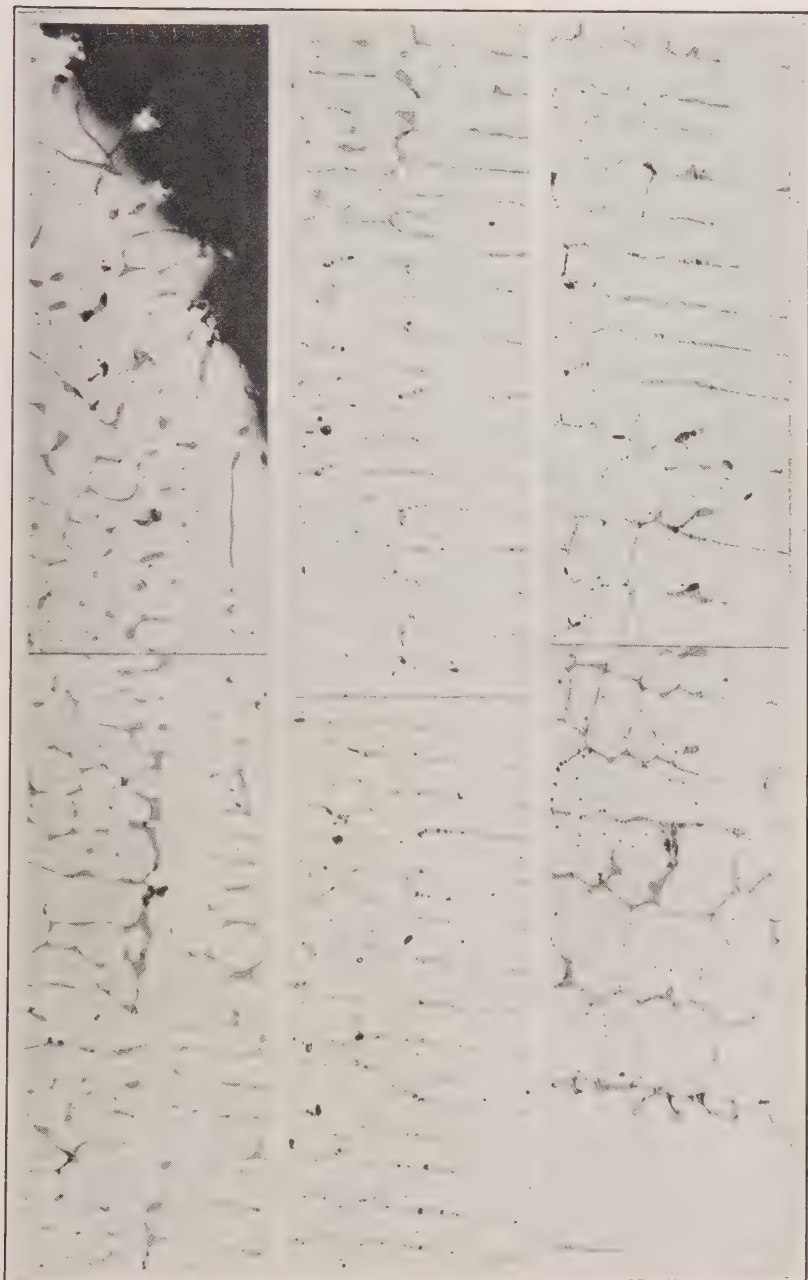


Fig. 48—Photomicrograph of Melt S-1. The Cell Wall Structure and Dendrites. The Sulphide is Located in Dendritic Filings. $\times 100$. Due to the Length of the Original Photomicrograph this Plate has been Divided into Three Strips. The Top of the Center Strip should Join the Bottom of the First Strip and the Top of the Third Strip should Join the Bottom of the Middle Strip.

Mechanism of Solidification of Iron and of Sulphide as Brought out by Sulphur Printing

Fig. 51 is an enlargement of the sulphur print of S-1. The dark areas correspond to the location of the sulphide. The relationship between the sulphide and the iron becomes now apparent at a glance. It is clear in the first place, that pure iron (barring any segregation effects due to dissolved FeS) crystallizes in dendrites, in the second, that iron sulphide solidifies in the fillings of the dendrites, as one would logically expect.

The sulphur printing process, of course, does not preserve details. Silver bromide paper saturated with dilute sulphuric acid is brought in intimate contact with the polished surface of a specimen. As a sulphide particle exposed at the surface is attacked by the acid, it liberates hydrogen sulphide, which immediately reacts with the silver bromide opposite the particle, forming black silver sulphide. The gaseous nature of the reagent implies ready diffusion from the place of its generation;—unless, therefore, the print is well timed, the stain created by the hydrogen sulphide is bound to spread considerably beyond the actual limits of the sulphide particle. In view of this the sharpness of outline exhibited by Fig. 51 is remarkable, especially when the sulphur print is viewed at high magnifications. (Fig. 54).

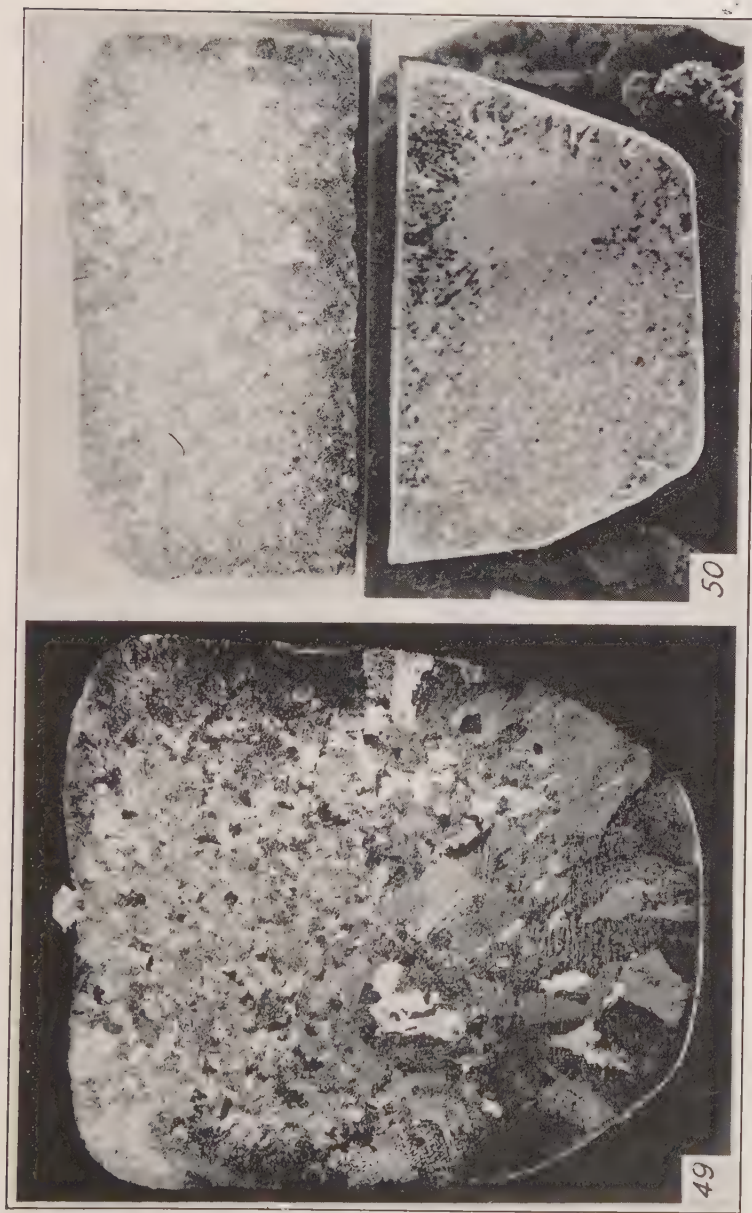
A Study of Etching Effects. Attempts of earlier investigators²⁴ to reveal dendrites in iron-sulphur alloys by the ordinary copper plating methods have failed, and this has been interpreted to mean that sulphur (or sulphide) is not dissolved in iron and hence cannot cause dendritic segregation.

The author succeeded, after many trials,²⁵ in revealing the dendrites by such methods. Fig. 53 shows the dendrites as brought out in S-1 by Le Chatelier's copper reagent (#2). They are the same as those shown by the sulphur print, only reversed (since the sulphur print gives a mirror image).

Closer study revealed that not only the sulphides but also the areas in the immediate neighborhood of the sulphides were free from copper. This can be accounted for by the existence of sulphide in solid solution in the iron, the less pure portions of the

²⁴See for example V. N. Krivobok's Thesis on the "Crystallization of Iron-Carbon Alloys," p. 78-9.

²⁵The able assistance of C. H. Chou in these trials is thankfully acknowledged.



The Macrostructure of High Sulphur Iron, S-1. Fig. 49—Original Grains, Etched 1½ Minutes in 10 Per Cent Nitric Acid, Vertical Illumination, $\times 312$. Fig. 50—Top Part Grains After Annealing S1-A. Bottom Part: Grains After Quenching, S1Q. Etched as Fig. 49. $\times 312$.



as Fig. 51 After Annealing and After Quenching. No Migration of Sulphide has Taken Place. $\times 3\frac{1}{2}$.

iron being located, of course, in the fillings immediately adjoining the sulphides. It is equally possible, however, that the sulphide interferes in some other way with the normal etching of the adjoining iron.

Sulphur printing with a 2 per cent sulphuric acid solution did not affect the sulphides perceptibly. The latter were blackened however after continued printing with a 10 per cent solution.

Formation of Small Globules. Turning now our attention to the tiny sulphide globules described in earlier pages, what can be said about their origin? There are two possibilities:

- (1) They are liberated from the iron on solidification of the latter,—but are, entangled in the rapidly congealing metal and prevented from reaching the main mass of sulphides, rejected to the fillings.
- (2) They are precipitated from the metal only after solidification of the latter and remain in situ if the metal is cooled fairly rapidly. On slow cooling they may have some opportunity to diffuse and to coalesce.

Definite conclusions cannot be arrived at on the basis of the limited observations made; inasmuch, however, as solid solubility of sulphide in iron is indicated, and inasmuch as such solubility, undoubtedly, decreases with a fall in temperature, the second possibility is not to be dismissed lightly.

Effects of Heat Treatment. As was mentioned in the review of the work of earlier investigators, the possibility has been entertained that iron sulphide, on heating of the iron, is redissolved by the iron, diffuses through it and finally, on cooling, is precipitated again “in between the crystal grains according to its habit.” Heat treatment changes the crystal grains of iron, as is well known; hence one would expect the sulphide, on annealing, to have migrated to new positions. In order to ascertain whether such migration takes place at temperatures employed in practice a part of S-1 was kept at 1760 degrees Fahr. (960 degrees Cent.) for one hour, then heated up to 1815 degrees Fahr. (990 degrees Cent.) and quenched, and another part annealed at 1760 degrees Fahr. (960 degrees Cent.) 2 hours and cooled very slowly in the furnace. The micro-distribution of the sulphide in the quenched



Fig. 53—Dendrites in S-I. Etched with Le Chatelier's Reagent. $\times 3\frac{1}{2}$. Fig. 54—Magnified Area of the Sulphur Print of Fig. 51. Note the Relative Sharpness of Dendrite Outlines. $\times 500$.

and the annealed specimens was found to be precisely the same as before heat treatment.

The relative grain sizes before and after heat treatment are shown in Figs. 49 and 50, the top portion of the latter shows the annealed half, and the bottom portion, the quenched half of the specimen. Quenching resulted, as is seen, in a marked grain refinement, while not much change in grain size is apparent in the annealed specimen. The grains, in either case, are different from the original grains, of course.

Figs. 51 and 52 permit a comparison of the sulphide distribution before and after heat treatment. The dendritic structure of the quenched half is seen to coincide with that of the original specimen even in detail and this despite the fact that oxidation necessitated the preparation of a new polished surface with attendant removal of a layer of sulphide and metal. Doubtlessly no migration whatever has taken place; the sulphide remained where it formed,—in the fillings of the original dendrites. The correspondence between the dendrites of the annealed half and the original specimen is not as perfect on account of the heavier layer of oxidized metal that had to be removed; still the correspondence is close enough to warrant the same conclusion.

This is of course what was to be expected. Indeed, why should sulphides migrate? With the increase of the dissolving power of the iron for sulphide at elevated temperatures, a small proportion of the sulphide might be dissolved, of course. But this would merely restore a condition existing in the melt when it originally reached the corresponding temperature, and would, perhaps, eliminate, for the time being, the tiny globules which were found in the iron. It could have no effect at all on a structure created at the temperature of solidification. Nothing short of remelting can be expected to change the distribution of the bulk of the sulphide, for this distribution is a function of the conditions of solidification only. Diffusion has to be reckoned with—but diffusion will take place only if there is a concentration gradient calling for it, or a special influence inducing it. No such gradient exists here, the metal throughout the ingot being saturated with all the sulphur it can hold in solution; nor is the presence of any special causes for diffusion indicated.

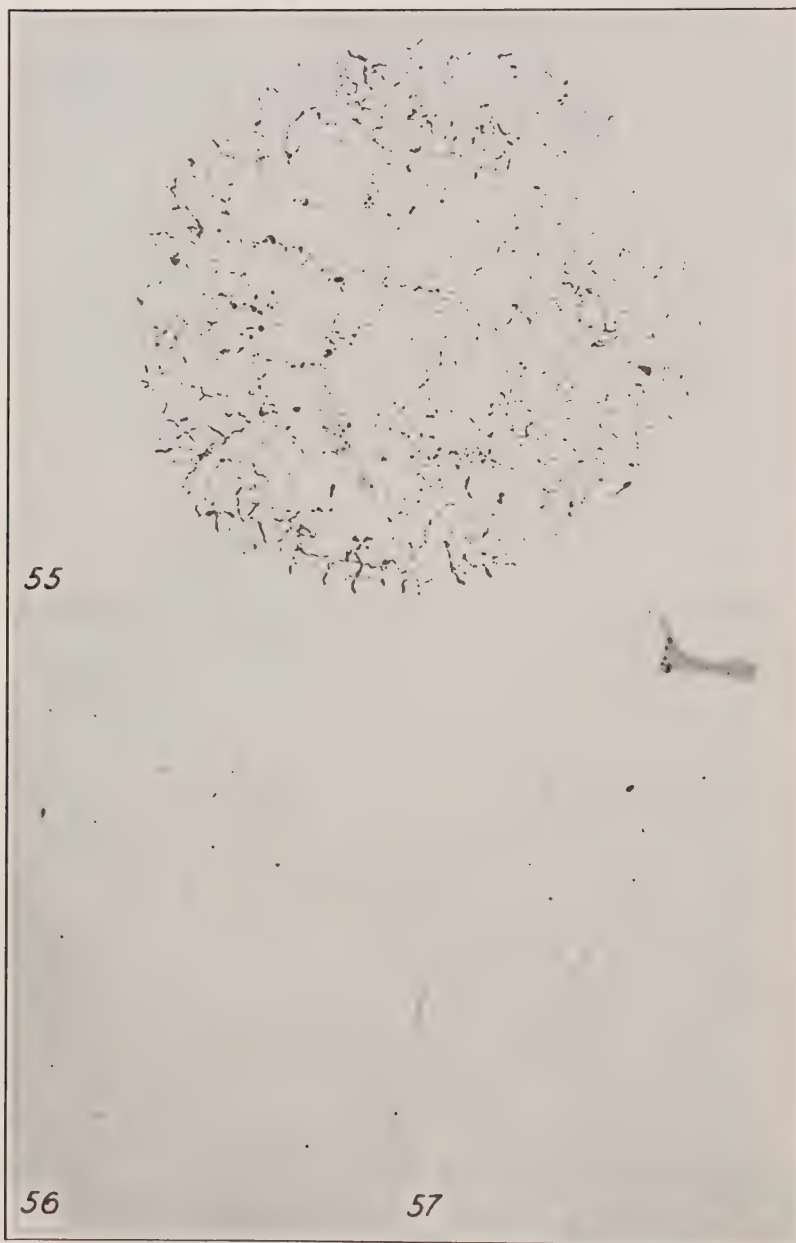


Fig. 55 S-3—Magnified Reproduction of Sulphur Print. $\times 3\frac{1}{2}$. Sulphide Inclusions in Low Sulphur Iron S-3. Fig. 56—Typical Appearance at 100 Diameters. Fig. 57—Tendency to Form Continuous Envelopes is Locally Shown, $\times 500$.

THE MEDIUM AND LOW SULPHUR MELTS

(S-3, S-4 and S-5)

The next melt prepared (S-3), containing in the neighborhood of 0.1 per cent sulphur, substantiated, in a general way, the conclusions arrived at from a study of the high-sulphur melt.

Sulphur Prints and Macrostructure. An enlargement of a sulphur print of the cross section of this melt is shown on Fig. 55. Corresponding to the lower percentage of sulphur the print appears much fainter than the prints of the previous case. Dendrites, at a first glance, appear not to be brought out; instead we observe the dark sulphide lines to circumscribe rather irregular areas. These areas correspond to the original dendritic grains of the ingot, now no longer existing, and the sulphide appears at the boundaries of these grains for the same reason that it appeared in the fillings of the dendrites in the previous case. These boundaries, in fact, are the last dendritic "fillings", as it were, since they represent the places where the last liquid material solidified. Closer inspection of Fig. 55 reveals that, after all, the dendritic outlines are brought out, though only faintly, being traced by tiny sulphide particles located in the fillings of the dendrites. There was not enough sulphide available, in the present case, to give a clearer picture of the dendrites.

Description of Inclusions. Microscopic examination of the unetched specimen at $\times 100$ shows the relative cleanliness of this melt (Fig. 56). The majority of the inclusions appear here in the form of small rounded sparsely scattered globules seldom exceeding 0.01 millimeters in diameter; occasionally more or less continuous extremely thin streaks are observed. Only at high magnification does the presence of considerable sulphide become noticeable. Minute globules of the order of 0.0001 to 0.001 millimeter in diameter are plentiful. The tendency of the sulphide to form envelopes is also exhibited. These envelopes are incomplete in most instances, appearing in the form of a series of interrupted small streaks, or in a series of globules as shown in Fig. 57 and Fig. 60. Not infrequently such incomplete "envelopes" can be traced for considerable distances along the specimen.

Occasionally hair-like sulphide lines connect the larger inclusions (Fig. 59), and these lines are, at times, so fine that they can be discerned only with the greatest difficulty even at magni-



Sulphide Inclusions in Low Sulphur Iron, S-3. Figs. 58 and 59—Extremely Thin Sulphide Lines are Seen to Connect Larger Sulphide Inclusions. $\times 2500$. Fig. 60—A Sulphide "Envelope" Formed by Tiny Globules. $\times 2500$.

fications as high as $\times 2500$ (Fig. 58). The significance of these sulphide "lines" is obvious from the preceding; they represent the junctions between two dendrites to which the sulphide, precipitated from solution, was rejected. The "lines" are thin because there is not enough sulphide to make them heavier.

The next lower sulphide melt (S-4) analyzed 0.033 per cent sulphur which corresponds to less than 0.1 per cent FeS. No inclusions could be found in this melt, even at the highest powers of the microscope, although specks suggesting inclusions were observed here and there. And, of course, in the last melt (S-5) which contained but 0.016 per cent sulphur no inclusions could be found either.

In both cases sulphur printing failed to discolor the silver bromide paper.

Solubility of FeS in Fe. It appears indicated that iron, in the absence of other elements, is capable of holding 0.02 per cent sulphur (or some 0.05 per cent FeS) in solid solution at atmospheric temperature. Solid solubility of sulphide in iron is also suggested by the effects of some etching reagents, notably the copper reagents, as was already shown, and of picric acid. [Le Chatelier and Ziegler (16)]

In any case this solubility is very small and gets still smaller in the presence of certain elements, such as manganese and oxygen. In ingot iron, for example, which contains but 0.02 per cent sulphur, sulphides are clearly recognizable, while in iron with this same percentage of sulphur, but free from oxygen none was observed.

Before leaving the subject of pure iron sulphide inclusions it might be well to consider a few aspects of these inclusions which the preceding photomicrographic studies failed to bring out. In particular, the system Fe-FeS and the question of the Fe-FeS eutectic, which is universally believed to exist, is deserving of attention.

THE SYSTEM Fe-FeS

The system Fe-FeS was first studied in detail by Treitschke and Tammann (23) who constructed the equilibrium diagram reproduced in Fig. 61. Later, K. Friedrich (50) checked the work of Tammann, using purer materials and experimenting with greater care. He found that Treitschke and Tammann were in

error in many important points and submitted the diagram shown in Fig. 62. Friedrich's work has been largely overlooked, later writers referring, in most instances, to the diagram of Treitschke and Tammann. We are, therefore, justified in giving our attention to this diagram first.

Treitschke and Tammann's Diagram. Not many steels are met with that carry over one per cent sulphur, (which corresponds

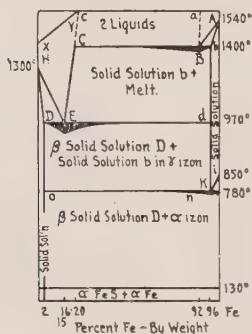


Fig. 61—Fe-FeS Equilibrium Diagram by Treitschke and Tammann.

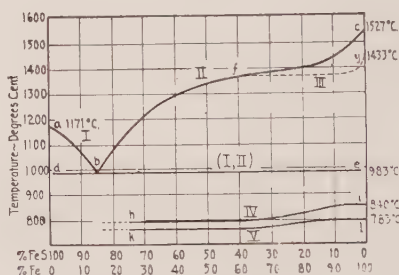


Fig. 62—Fe-FeS Equilibrium Diagram by Friedrich.

to about 2.75 per cent FeS). It is, therefore, only the extreme right portion of Tammann's FeS-Fe equilibrium diagram that is of practical interest. According to this portion of the diagram, and explanatory statements in the original text, melts containing from 0 to 4 per cent FeS form solid solutions of the composition of the melt. These solid solutions persist until they reach the line ik (temperature range 850 to 750 degrees Cent.) where separation of pure alpha iron takes place, the remaining solid solution becoming richer and richer in FeS until a 7 per cent FeS content is reached. The solution then breaks up into FeS and beta iron, according to Tammann. Lastly, at 128 ± 5 degrees Cent. an allotropic transformation of beta-FeS into alpha-FeS takes place, a transformation which had been noted already by Le Chatelier and Ziegler (16) in the course of dilatometric observations.

Tammann's conclusions are, clearly, not in accord with the facts. The observations of the author, and of many other investigators, if properly interpreted, show that iron while passing from the liquid to the solid state loses its dissolving power for most of the sulphide which, accordingly, is rejected to the dendritic

fillings and to the boundaries between adjoining iron dendrites. It will be remembered that inter-dendritic sulphide envelopes were obtained with a sulphur concentration as low as 0.1 per cent, corresponding to some 0.28 per cent FeS. We are justified then in concluding that iron, immediately after solidification is capable of dissolving materially less than 0.3 per cent FeS and surely not up to 4 per cent FeS, as is suggested by Treitschke and Tammann.

Contrary to accepted views [Levy (29), Ziegler (31), Röhl (37)], it does not follow from Treitschke and Tammann's diagram that sulphide inclusions are made up of a Fe-FeS eutectic.

Treitschke and Tammann, in fact, make no mention of a Fe-FeS eutectic for the case of iron containing less than 4 per cent FeS which is the only case important in practice.

Diagram of Friedrich. The eutectic nature of iron sulphide inclusions follows, however, from the diagram of Friedrich (95) which, in the opinion of the writer, is a far more accurate and reliable diagram than the one just described (Fig. 62). In fact, Friedrich has shown (50) that many of the complications pictured by Tammann were attributable to the presence, in his melt, of oxide.

The main points of Friedrich's diagram as contrasted with Treitschke and Tammann's diagram are:

- (1) There is no separation into phases of the liquid melt.²⁶
- (2) Solid solutions of FeS in Fe and Fe in FeS (of noticeable concentration) are absent.
- (3) Practically pure iron separates, in iron-rich melts (and practically pure sulphide in sulphide-rich melts) until the melts reach the eutectic composition: —(15 per cent Fe, 85 per cent FeS). This eutectic solidifies at 1800 degrees Fahr. (983 degrees Cent.)
- (4) No subsequent changes of importance are noticeable, the thermal effects at 840 and 783 degrees Cent. being ascribable to the allotropic changes of the iron.

The author's observations, in a broad way, are in accord with Friedrich's tentative conclusions, except for the fact that no evidence of a Fe-FeS eutectic was found.

²⁶This was recently substantiated by Bogitch (53).

The Fe-FeS Eutectic. This eutectic, in sulphide inclusions, has never been seen by other investigators either.

Thus, G. Röhl (37) states:

“... this eutectic is so infinitely fine that it is not possible to resolve it into constituents when cooled normally, even when high magnifications are employed.”

M. Ziegler (31) admits that:

“En examinant la surface de l'eutectique fer-sulfure dans le fer et l'acier sous un agrandissement aussi fort que possible, il ne m'est pas arrivé une seule fois d'y observer du fer d'un caractère eutectique, tant ce eutectique est fin.”

Both Ziegler and Röhl examined the structure of melts containing in the neighborhood of 85 per cent FeS (the theoretical amount for the eutectic) and both present pictures of this eutectic the structure of which is quite well developed. Curiously enough they seem to find it quite in order that the eutectic, here, is visible at relatively low magnifications, although, according to their own testimony, this eutectic is ordinarily exceedingly fine by habit.

As the author sees it we have either no eutectic at all when dealing with low percentages of FeS, or, what is more probable, the components of this eutectic divorce and coagulate with such readiness (in the presence of excess iron) that the structure cannot be preserved, even on rapid cooling.

4. *Manganese Sulphide (+ Iron Sulphide) and Iron*

It appeared desirable to consider separately the following three cases:

- (1) Sulphur in excess of the theoretical amount necessary to form MnS.
- (2) Manganese and sulphur in the exact proportion to form MnS.
- (3) Manganese in excess of the theoretical amount called for by MnS.

Three melts were prepared in accordance with the above scheme: S-6, S-7 and S-8, the average analyses of which, in terms of MnS and excess Mn and S, were found to be as follows:

| | | | | | | |
|-----|-----|-------|-----|-------|----|-------|
| (1) | S-6 | | MnS | 1.61% | S | 0.16% |
| (2) | S-7 | | MnS | 1.71% | Mn | 0.45% |
| (3) | S-8 | | MnS | 1.09% | Mn | 5.7 % |

Elemental sulphur and manganese were charged into the electrolytic container in powdered form, layers of sulphur alternating with layers of manganese. The sulphur and manganese were thus in contact with each other and with the iron as well, and ample opportunity was given for these elements to establish preferred unions.

THE EXCESS SULPHUR MELT (S-6)

Distribution of Manganese and Sulphur. The excess sulphur of S-6 was expected to form FeS which either would appear as a separate constituent alongside with MnS, or else form a solid solution with MnS if such solutions existed. The MnS, in view of its undisputed insolubility in iron and its inferior density, would, furthermore, be expected to float to the top of the melt, leaving the bottom part of the ingot relatively free of sulphide. The top portion of the resulting ingot, indeed, was found to be very much richer in manganese than the bottom part, the sulphur, however, strangely enough, did not seem to follow the manganese. The analyses are given in Table II. Recalculated in terms of MnS and FeS, and excess manganese, we have:

| | Top fourth | Bottom fourth |
|-----|------------|---------------|
| MnS | 2.15% | 0.92% |
| Mn | 0.11% | ... |
| FeS | ... | 1.02% |

Such calculations do not apply to the actual case as is evident already from the fact that notable amounts of FeS were observed near the top of the ingot. This means that a considerable proportion of the sulphur allotted to the manganese is, in fact, combined with the iron. The percentage, then, of free metallic manganese must be much higher than would appear from the calculations. This in turn makes the presence of FeS still more of a puzzle.

Description of the Inclusions. Figs. 63-66 illustrate the representative structures observed in passing from the top of the ingot to the bottom. The contrast between the top and bottom structures (Figs. 63 and 66) is striking,—the transition is, however, very gradual as is illustrated by the intermediate Figs. 64

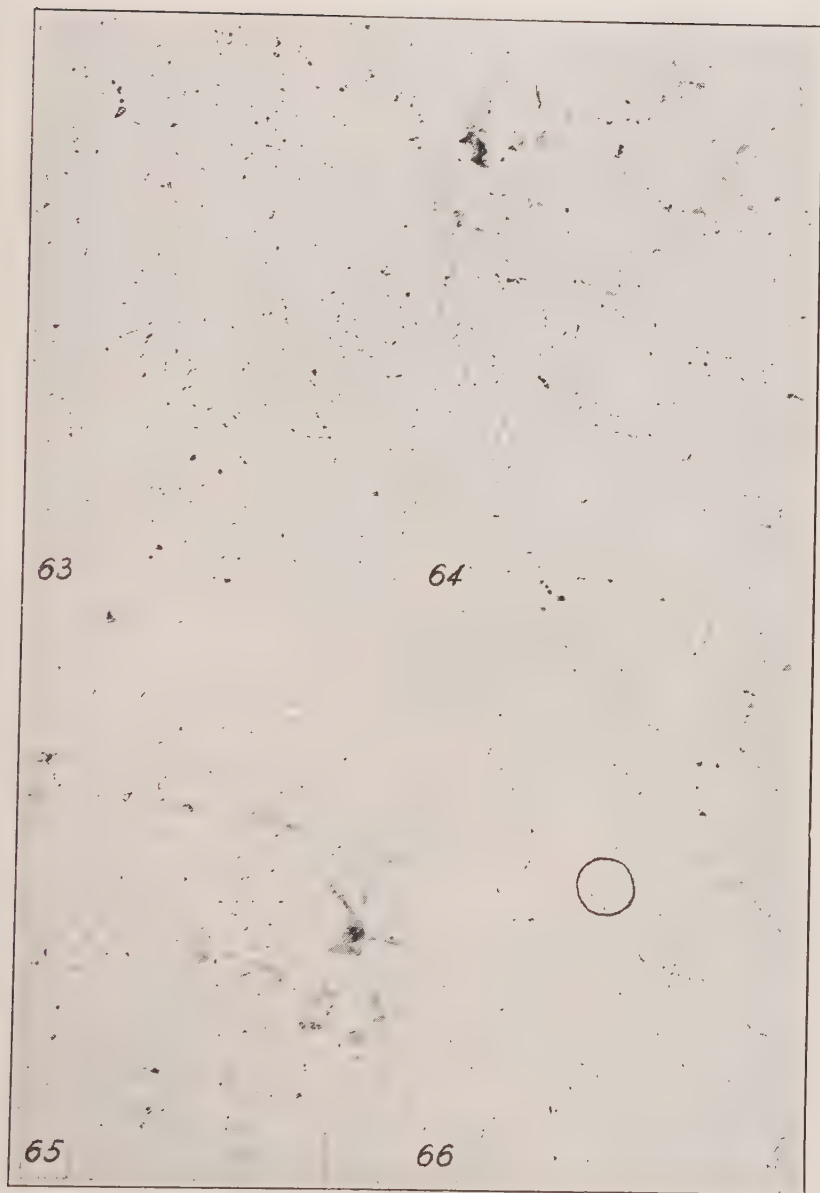
and 65. Near the top we have a structure first depicted by Le Chatelier (16), and later described in detail by Arnold and Bolsover (38). Two constituents are distinctly discernible under the microscope (Fig. 67). A pale yellow constituent, concentrated mainly in the clear cut though interrupted streaks or cell walls, and a dove gray one appearing in the cells in the form of tiny dots or globules which grow and become somewhat elongated on approaching the cell walls. The yellow constituent is, without doubt, FeS or a solid solution rich in FeS, while the gray one is either MnS or a solid solution rich in MnS. The brilliancy of these two constituents is so alike that a differentiation of them on a photographic reproduction is impossible unless a special color filter is used in making the picture. The author used a red filter which renders the gray sulphides darker than the yellow ones. Photomicrographs prepared in this manner are presented on Figs. 68 and 69, which serve to illustrate the observed relationships in further detail.

The Fe-MnS Eutectic. If we were shown the middle portions of the meshes depicted in Figs. 63 and 67, and were asked what the structure signifies we would be tempted to say that it represents a eutectic of some sort or another. In the opinion of Arnold and Bolsover (38), these groups of manganese sulphide dots and dashes radiating from a center "form strong evidence of the presence of a eutectic of ferrite and manganese sulphide existing whilst the steel was in a fluid condition and which falls out on (or possibly before) the solidification of the steel in rounded masses, which eventually decompose into their eutectic components. In all big ingots it is probable that the small manganese sulphide particles of the eutectic mixture ball up into relatively large masses and the eutectic structure disappears."

We cannot agree with Arnold in his notion that a eutectic which solidifies earlier than one of its components can exist; we must agree, however, with the observation that the structures exhibited are, indeed, suggestive of a eutectic.

A eutectic implies two things:

- (1) Simultaneous crystallization of its components.
- (2) Constancy of composition (and of the temperature of solidification).



Variation in Sulphide Structures of the Ingot S-6. Fig. 63—Structure Near the Top. $\times 100$. Fig. 64—Structure Toward the Middle (About $\frac{1}{2}$ from the Top). $\times 100$. Fig. 65—Structure at the Middle. $\times 100$. Fig. 66—Structure Near the Bottom. $\times 100$. Note: Figs. 64 and 65 were Photographed After Annealing and Quenching of the Ingot. These Treatments did not Affect the Structure However.

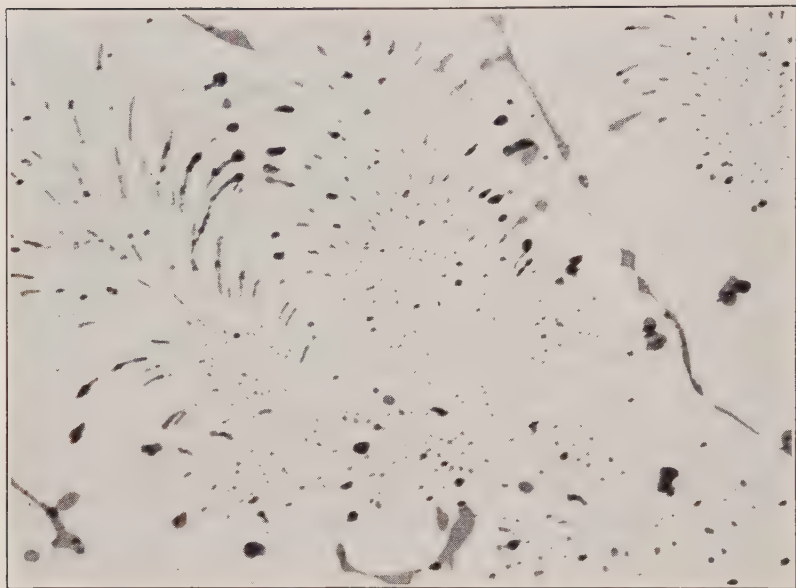


Fig. 67—"Dots", "Dashes" and "Cell Walls" of FeS-MnS Inclusions in Melt S-6. $\times 300$.

Simultaneous crystallization of the iron and the gray sulphides is clearly indicated.

What about the constancy of composition, especially the constancy of the temperature at which solidification takes place? The centers of the "dot clusters" mark clearly the centers from which crystallization started. The sulphide dots in the neighborhood of these centers are usually small and distributed uniformly. As we proceed toward the periphery of the clusters the dots become larger and more widely spaced, and eventually assume elongated shapes arranged in a fan-like manner. The relative amounts of sulphide and iron appear to remain constant which would tend to support the existence of a eutectic. The composition of the individual sulphide particles, however, does not seem to remain constant (as is suggested by faint differences in the color of the globules in the center and that of the ovoids nearer to the periphery). The temperature of solidification, then, cannot remain constant throughout the solidification period of any one mesh, either.

What we have is probably not a eutectic in the strict sense of the word. We have simultaneous crystallization of two components

with a gradual change in composition of both. The iron gets richer in dissolved impurities, probably; while the sulphide gets richer in FeS content. The cell walls, as in the case of the pure iron sulphide melts, represent the last portions to solidify and mark, consequently, the dendritic fillings and inter-dendritic boundaries.

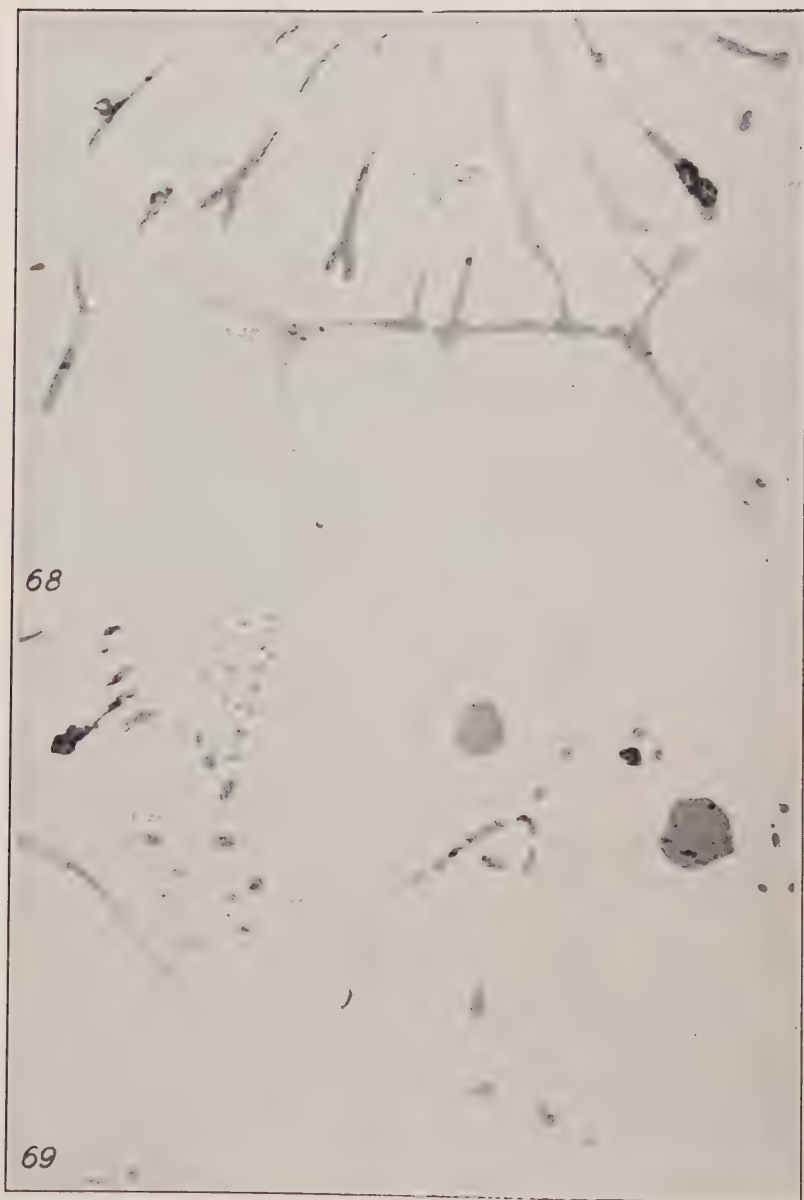
The theory of simultaneous crystallization of sulphide and of iron implies the presence of sulphide in the axes of the metal dendrites as well as in the fillings. This is verified by the sulphur print of the top section of S-6 (Fig. 71). Suggestions of dendrites are discernible here and there in the print,—on the whole, however, the picture is confused.

Constitution and Occurrence of Inclusions. Let us examine now the probable constitution of the sulphide inclusions. The gray sulphide globules can hardly be pure manganese sulphide. In the first place these globules were apparently in solution in the iron while manganese sulphide is supposedly insoluble in iron; in the second, they have a solidification point not unlike that of iron, while MnS, according to many, solidifies much earlier. The melting point of MnS is still being disputed, however; it also might be contended that the sulphide globules seen are the products of a reaction of Mn and FeS—both of which are dissolved in the iron—a reaction which takes place only at the instant of solidification of the iron.

Such contentions fail to account for the slight but consistent change in color of the gray sulphides. This consistent change in color can be caused only by a similarly consistent change in composition,—a change which, by the way, terminates in pure or nearly pure FeS. There is hardly any doubt that we are dealing here with a series of solid solutions of FeS in MnS. The higher the FeS content of the solution the lower its melting point and the lighter its shade.²⁷ And while MnS is insoluble in molten iron, $\text{MnS} + \text{FeS}$ or its equivalents may well be.

The series of the FeS-MnS solid solutions is not a complete one; as a more or less abrupt change in color from a very pale gray to a pale yellow takes place at some intermediate concentration. This change is illustrated by Figs. 68 and 69. The darker constituent is pale gray, the lighter pale yellow. Not all the cell walls show a duplex structure—a few appear yellow throughout, and in some cases even globules of uniformly yellow FeS can be seen in

²⁷It must be noted that the differences in shade are apparent, to a trained eye, only in a well prepared specimen and only after a prolonged study of the specimen.



Figs. 68 and 69—Duplex Structure of the Cell Walls and Yellow and Gray Inclusions in Melt S-6. Red Filter. The Lighter Areas are Yellow Sulphide, the Darker—Gray Sulphide. $\times 500$.

close neighborhood of gray MnS-rich globules as for example in the center of Fig. 69.

This latter relationship becomes increasingly more frequent as we proceed toward the bottom of the ingot. The eutectic clusters of fine dots become less and less frequent, being gradually replaced by an apparently irregular aggregate of much larger globules which, in turn, gives way to globules arranged in orderly patterns, fully analogous to the continuous cell wall patterns, of S-1 (Figs. 58-60). At the same time the color of the inclusions changes. Lighter grays become the rule and more and more yellow becomes apparent.

The orderly arrangement of the sulphide globules suggests that they are located in the dendritic fillings. Sulphur printing proved this to be the case.

Duplex Structure of the Inclusions. Reference was already made to the duplex structure of the cell walls in the top portion of the ingot. A similar joint occurrence of faint gray and pale yellow constituents is not infrequent in the rounded globules prevalent in other parts of the ingot. Most commonly a gray globule is seen to be surrounded by a yellow envelope; occasionally, however, more complex structures, such as depicted in Fig. 70, are met with.

It can be predicted that heat treatment of such inclusions will result in a great variety of structures depending on the nature of the treatments. Quenching, probably will preserve a uniform solid solution, supersaturated at atmospheric temperature; subsequent moderate annealing will result in a separation of the constituents of the solution, perhaps in a Widmanstätten pattern or a related form; prolonged annealing, in complete divorce.

Effects of Heat Treatment. Heat treatment of the specimen did not result in any changes in the distribution of the inclusions, as is seen from Figs. 64 and 65.

Whether or not changes had taken place in individual inclusions could not be ascertained definitely since inclusions studied prior to heat treatment could not be preserved for examination after the treatment. Oxidation, attendant to annealing, introduced in fact more complications than those which arose from the necessity to prepare a new polished surface for examination. The changes effected by oxygen will be discussed in the next chapter.

Apart from these extraneous phenomena the appearance of the inclusions after treatment supported the contention that such

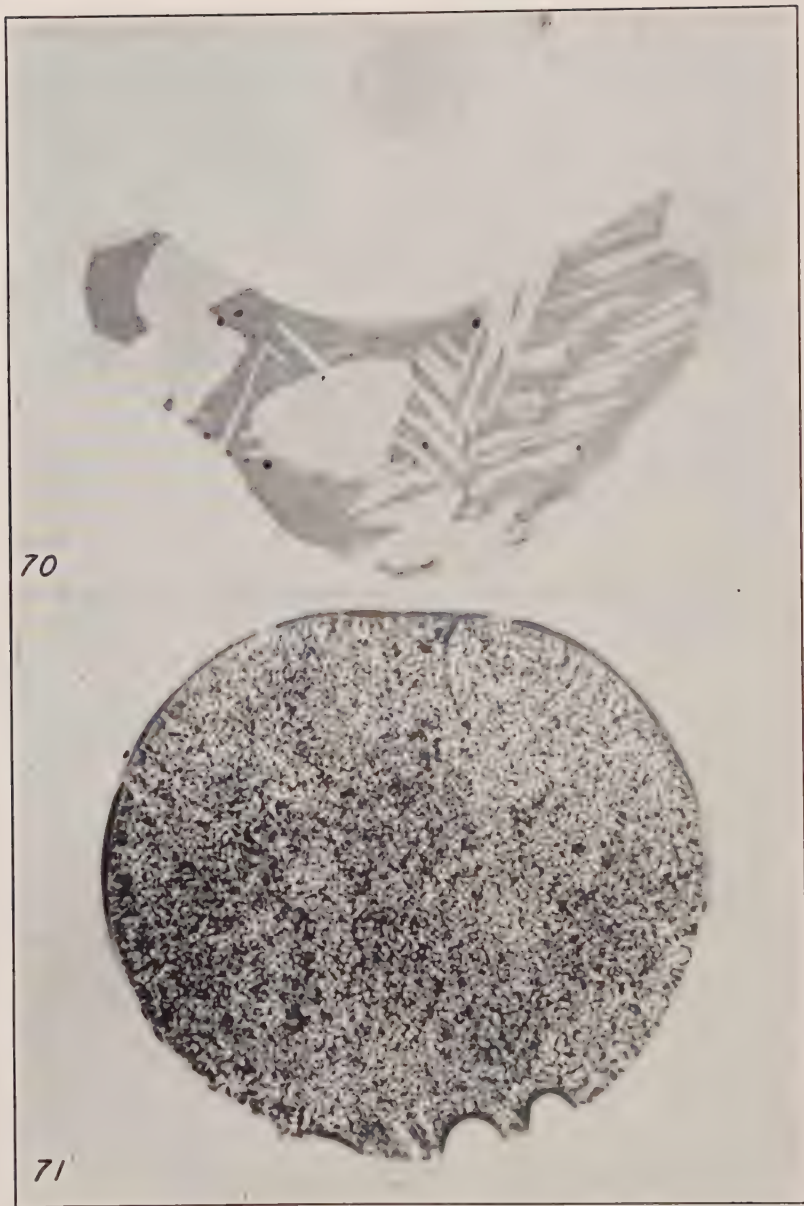


Fig. 70—Melt S-6 (S-6A). Annealed. Red Filter. Widmanstätten Patterns in FeS-MnS Inclusions. The Yellow Sulphide Appears Light. $\times 2500$. Fig. 71—Melt S-6. Sulphur Print of the Top Section. Note the Confused Structure. $\times 3\frac{1}{2}$.

treatment has an influence on their structures. This will become apparent when the evidence of Chapter IV is presented.

Identification Tests. It appeared of interest to ascertain whether inclusions exhibiting faint color differences would behave differently under the action of chemical reagents. The typical group pictured in Fig. 73 was selected for a first trial. The largest inclusion in the middle of the photograph is pale gray, the two globules immediately to the left and to the right have a yellowish rim while the two globules further below and to the right are again uniformly pale gray. The elongated inclusion above is uniformly pale yellow and the two inclusions in the right upper corner of the picture are uniformly yellow and uniformly gray respectively. Fig. 74 shows the same inclusions after five minutes etching in a 10 per cent solution of chromic acid in water—a solution recommended by Campbell and Comstock (49) for the identification of manganese sulphide inclusions. Only one of the gray inclusions succumbed to the attack of this reagent, and one—the large inclusion—showed signs of weakening.

Next sulphur printing for 20 seconds (using a 2 per cent H_2SO_4 solution in water) was resorted to. This treatment eliminated successfully all gray inclusions (Fig. 75,) leaving the yellowish ones fully intact, even the narrow yellow rims of the duplex inclusions. The action of sulphur printing is further illustrated by Fig. 72. Only the pure or nearly pure FeS is seen to be preserved.

Sulphur printing for 20 seconds with a 2 per cent H_2SO_4 solution apparently destroys all sulphide solid solutions preserving merely the pure FeS , while chromic acid attacks only the solid solutions rich in manganese sulphide. Further tests substantiated these conclusions. A means of differentiation between manganese-rich and manganese-poor sulphide solutions is thus afforded.

Unfortunately, sulphur printing cannot serve as a qualitative test for mixed sulphide inclusions, since it destroys, as was seen in Chapter II, solid solutions of oxides also.

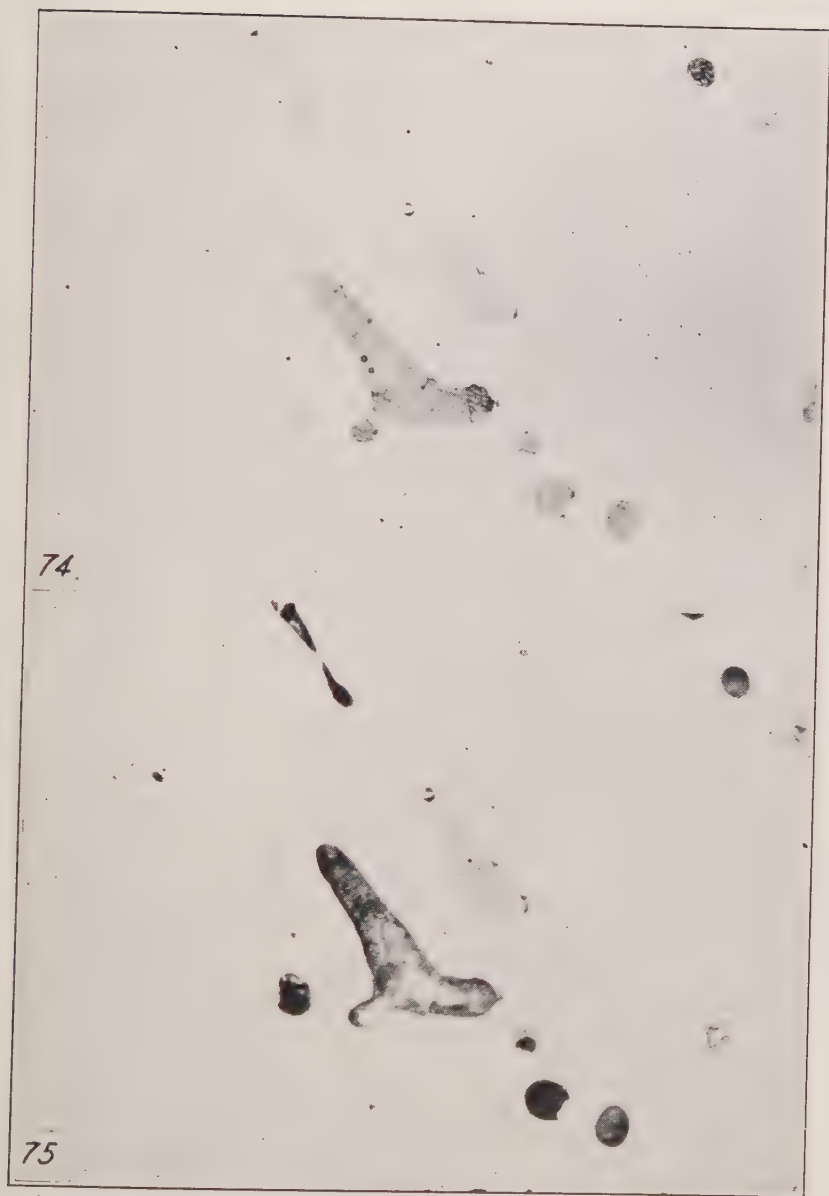
THE MELT WITH THE THEORETICAL AMOUNT OF MANGANESE

(S-7)

Study of a longitudinal section cut through this melt revealed the presence of three more or less distinct zones grading into one



Fig. 72—Effect of Sulphur Printing on FeS-MnS Inclusions in S-6. All Gray Sulphides are Destroyed, the Yellow Ones Only Survive. $\times 500$. Etching Studies on FeS-MnS Inclusions in S-6. Fig. 73—A Selected Spot (Within Fig. 66). Red Filter. Yellow, Gray and Duplex Inclusions. $\times 500$.



Etching Studies on FeS-MnS Inclusions in S-6. Fig. 74—The Same Spot as Shown in Fig. 73. After Etching for 10 Minutes with 10 Per Cent Aqueous Chromic Acid. The "Grayest" Inclusions are Attacked. $\times 500$. Fig. 75—The Same Spot After Sulphur Printing for 20 Seconds, Using 2 Per Cent Aqueous Sulphuric Acid. Only the Yellow Sulphide Survived. $\times 500$.

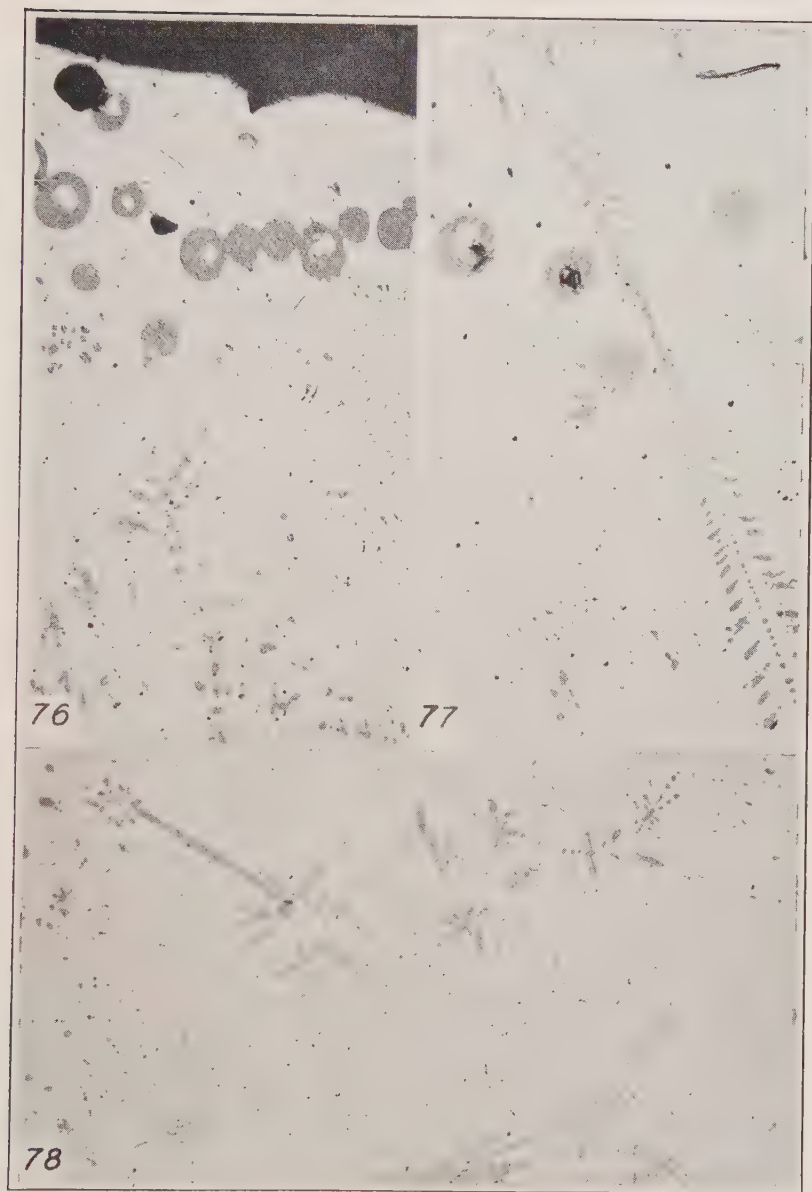
another. The top zone shows dendritic forms of a rich dove gray constituent in a matrix of the eutectic-like "dot" aggregate described earlier. The middle zone exhibits only the fine "dot-type" structure while the bottom zone contains larger sulphide globules, much like the ones of the bottom portion of the previously described melt S-6.

Description of the Inclusions in the Top Zone. A concentration of manganese toward the top of the ingot has, clearly, been effected. Note the perfect dendritic forms found near the top of the ingot (Figs. 77-78). They must have crystallized from the melt prior to the solidification of the latter. How could they otherwise have developed and grown undisturbedly to the extent shown? It appears to the writer that in these dendrites we meet for the first time pure MnS, although it is, of course, quite possible that even these dendrites contain some FeS in solid solution.

In any case it is evident that pure MnS has a solidification point higher than that of iron, because (1) sulphide dendrites consisting essentially of MnS have solidified before the iron solidified, and (2), the melting point of MnS can only be lowered by admixture of FeS.

Why did these dendrites concentrate near the top of the ingot? Did segregation take place already in the liquid melt, a layer rich in the dissolved components necessary for the formation of MnS forming at the top of the melt; or did the dendrites float to the top after having formed in lower regions of the melt? The manner of occurrence of the large rounded globules of MnS (Fig. 76) found at the surface of the melt suggests definitely that they were not born there. The fact that these globules show only faint beginnings of coalescing suggests further that they were essentially solid at the time they reached their present location. The dendritic crystals do not seem to form a definite system, but show rather a haphazard distribution. In all probability the concentration of MnS toward the top of the ingot took place both due to segregation in the melt itself, and due to a floating to the top of solid MnS. It is possible that on reaching their present location the MnS dendrites continued to grow extracting some of the MnS from their immediate surroundings. This, in fact, is suggested by the absence of the "eutectic" structure in the immediate neighborhood of some of the dendrites.

The pseudo-eutectic, here, differs from that of the previously



"Manganese Sulphide" Dendrites in S-7. Fig. 76—Dendrites, Dot-Clusters and Semi-Coalesced Large Globules at the Very Top of the Ingot. $\times 100$. Fig. 77—Another Spot Near the Top. $\times 100$. Fig. 78—Dendrites Further Below the Top. $\times 100$.

described melt (S-6) merely in showing a much smaller proportion of elongated sulphide particles. These latter, as was explained earlier, develop near the periphery of the clusters and signify increasing FeS content in the sulphide solutions there. Their decrease in prominence, in the presence of a larger excess of manganese, was to be expected.

Yellow sulphide is essentially absent, high powers revealing only two or three duplex inclusions over the entire area of zone 1.

Inclusions in the Middle and Bottom Zones. The middle and bottom zones exhibit no novel features. Of interest is, perhaps, one aspect of the pseudo-eutectic not brought out before. Near the walls of the ingot, where dendrites usually develop with especial clearness, the pseudo-eutectic is seen to be located in dendritic fillings (Fig. 79). This suggests that the pseudo-eutectic solidifies at a temperature slightly lower than pure iron. This is in line with what one would logically expect (even of a pseudo-eutectic) and serves to disprove Arnold and Bolsover's notion of the high melting point of this eutectic.

Yellow sulphide makes its appearance at the peripheries of the eutectic clusters of the middle zone; is, however, less plentiful than in S-6. Duplex inclusions are frequent.

In the bottom zone individual sulphide globules are larger (Fig. 80), the proportion of yellow sulphide is more marked, and even pure yellow inclusions are occasionally seen.

The Sulphur Print. The entire story of this melt can be seen at a glance from an enlargement of the sulphur print of a longitudinal section of the ingot (Fig. 81). At the bottom we have the familiar light iron dendrites outlined by dark sulphide fillings. The iron solidified first, the sulphide last. In the middle zone the structure is confused,—iron and sulphide solidifying essentially simultaneously. At the top we see again dendrites,—this time, however, black dendrites in a light matrix. These are sulphide dendrites which solidified before the iron which here occupies the fillings.

Etching Effects of Chromic Acid. It was deemed desirable to check the etching effects of chromic acid observed in the case of the previous melt (S-6), and at the same time to observe how easily the manganese-rich dendrites would succumb to this reagent. The results were somewhat unexpected. The fine sulphide particles of

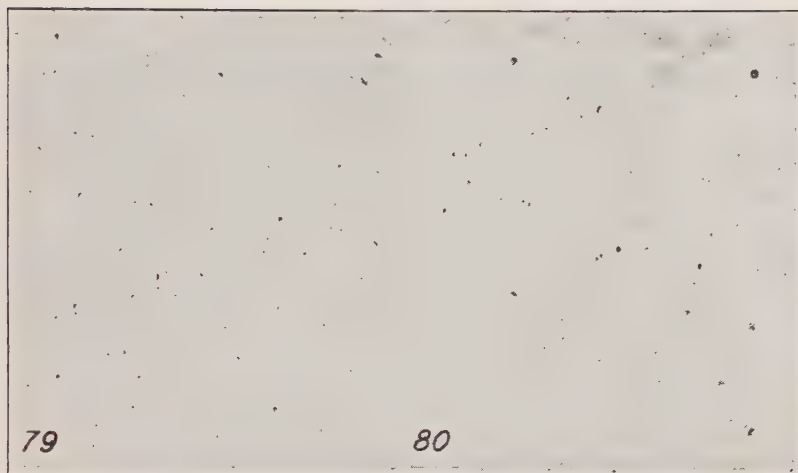


Fig. 79—The Fe-MnS "Eutectic" in Dendrite Fillings in the Upper Portion of the Ingot. (Near a Side Wall.) $\times 100$. Fig. 80—Inclusions in the Lower Portion of the Ingot. They are Larger and Appear to be Distributed at Random. $\times 100$.

zone 1 were darkened, the larger particles, however, and the dendrites, showed merely faint signs of attack. No etching effects at all were discernible in the other zones. On repetition of the treatment the etch of zone 1 was found to have deepened, in zone 2 the fine "eutectic" inclusions were partially attacked; the rest of the inclusions, however, showed no signs of weakening.

What is the explanation for this? It is well known that the association in which a given metal or mineral is present governs to a marked degree the behavior toward etching reagents of this metal or mineral. If a metal, capable of being attacked by a certain reagent, is embedded in another metal more susceptible to that reagent, then, upon etching, it will generally be found that only the latter metal is attacked. The activity of a reagent is somehow concentrated at places more susceptible to attack, and this is precisely what happened in the present case. The inclusions of the bottom zone are freest from manganese and therefore least susceptible to chromic acid etching. Accordingly the reagent concentrated its efforts on the easier prey. There may have been, of course, other reasons for the failure of the etching treatment; the case merely emphasizes how unreliable identification methods based on etching effects alone are.

The fact that the large MnS particles, notably the bulky

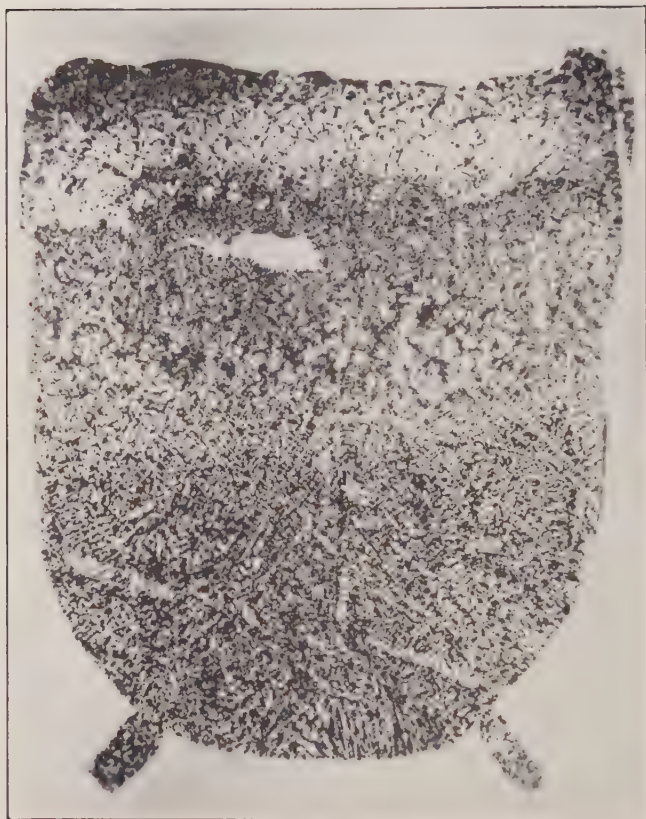
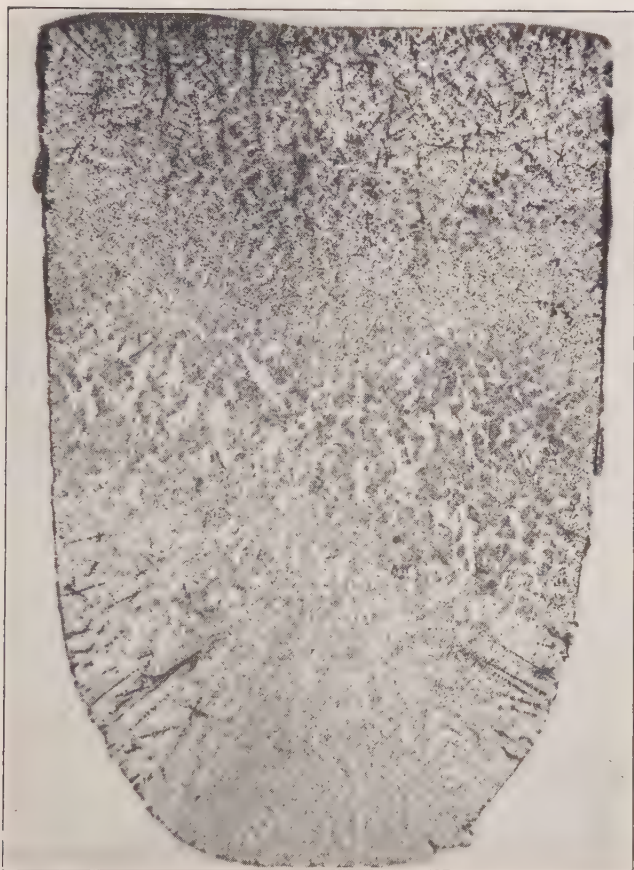


Fig. 81—Reproduction of the Sulphur Print. Note the Black Manganese Sulphide Dendrites Near the Top, the Confused Structure in the Upper Third, and the Sulphide Location in Dendritic Fillings in the Lower Half. $\times 3\frac{1}{2}$.

dendritic forms, survived an etching treatment which was directed primarily against them illustrates another important point which is not always borne in mind. The relative size of inclusions is a factor that cannot be neglected. A larger inclusion of "weaker" composition may survive an attack which destroys a smaller chemically "stronger" inclusion.

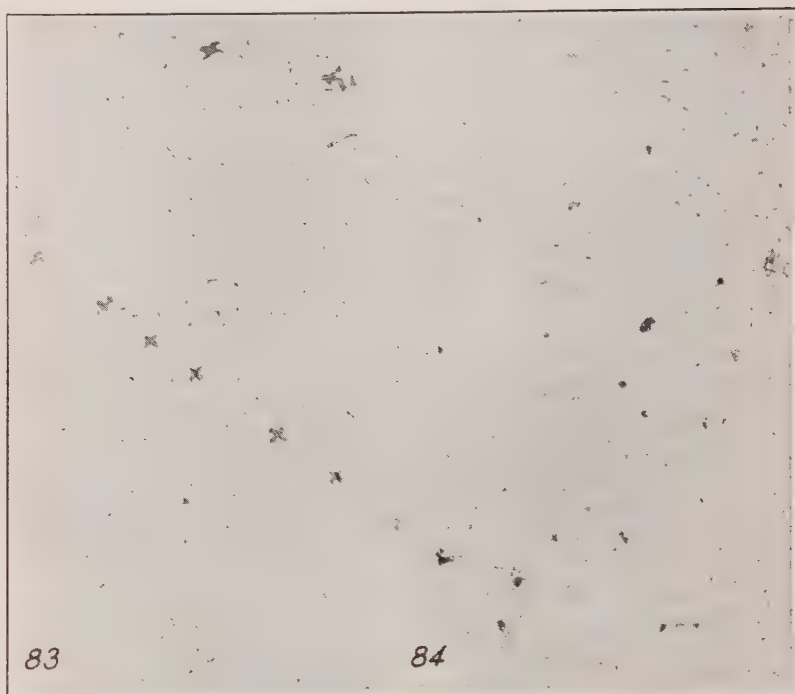
THE MELT WITH A LARGE EXCESS OF MANGANESE (S-8)

Description of the Inclusions. The story of the last melt (S-8) is told by the sulphur print reproduced in Fig. 82. Except



The Sulphide Melt S-8. Fig. 82—Reproduction of the Sulphur Print. $\times 3\frac{1}{2}$.

for the dark MnS dendrites the print exhibits the confused structure typical for the uniform mixture of metal and of sulphide. We expect to find the pseudo-eutectic structure throughout the entire melt and we do. This eutectic here is especially fine—a magnification of $\times 500$ generally being necessary to bring it out, instead of $\times 100$ as in the cases described before (Fig. 84). In the presence of so large an excess of manganese as is available in the melt under discussion but very little FeS can form and alloy itself with the manganese sulphide. The melting point of this FeS-poor sulphide will, therefore, be relatively high, and it is quite possible that it was precipitated in the form of a cloud of fine particles already



The Sulphide Melt S-S. Fig. 83—Section Through a Set of Branches of an MnS Dendrite. $\times 100$. Fig. 84—The Extremely Fine Dot Structure Formed in the Presence of a Large Excess of Manganese. $\times 500$.

in the liquid metal, most probably at a time when the metal already had acquired a viscosity which prevented the rising toward the surface of these particles.

It is significant, perhaps, in this connection, that the finest particles were found at the bottom of the ingot.

A few sulphide dendrites are seen to be located along the ingot walls near the bottom. This in no way contradicts the conclusions drawn about the formation at the top and the floating to the top of a melt of such dendrites. The manganese, in the present melt, was charged at the bottom of the container: the bulk of it is, nevertheless, concentrated at the top. The dendrites at the bottom walls, just referred to, suggest by their position that they were held in place by the walls of the crucible (or by the metal which solidified near the cooling walls). Fig. 83 illustrates typical cross sections of MnS dendrite branches.

THE IRON-MANGANESE-SULPHUR SYSTEM

The System FeS-MnS. The first FeS-MnS equilibrium diagram was worked out by G. Röhl (37). It is reproduced, in its original form, on Fig. 85. According to Röhl a compound of the

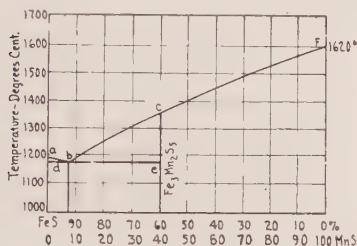


Fig. 85—The First FeS-MnS Equilibrium Diagram as Worked Out by G. Röhl.

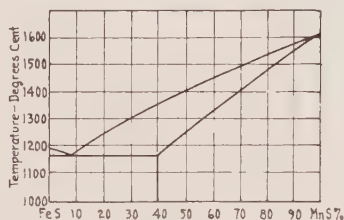


Fig. 86—The Corrected FeS-MnS Diagram as Given by McCance.

composition 60 per cent FeS and 40 per cent MnS, corresponding to the formula $\text{Fe}_3\text{Mn}_2\text{S}_5$, is formed. Unlimited solubility exists between this compound and excess manganese sulphide. On the other hand, if iron sulphide is in excess, a eutectic of FeS (or of Fe-FeS) and $\text{Fe}_3\text{Mn}_2\text{S}_5$ appears (7 per cent MnS, 93 per cent FeS). As was correctly pointed out by McCance, the thermal and microscopical data of Röhl imply in no way the existence of the compound just referred to. The point corresponding to a composition of 40 per cent MnS and 60 per cent FeS merely indicates the limit of solid solubility of MnS in FeS. The corrected diagram, as given by McCance (41), is reproduced in Fig. 86, and is in good accord with the findings of the author. The high melting point of manganese sulphide was verified and the existence of solid solutions between FeS and MnS substantiated. It was further found that there exists a continuous series of solid solutions beginning with pure MnS and ending with a limiting solution of a composition fairly rich in FeS. The yellow sulphide of the author should correspond to the eutectic with 7 per cent MnS shown in Röhl's diagram. Having found no conclusive evidence of a eutectic structure the writer is inclined to believe the inclusions to be pure FeS. The components of this eutectic, it appears, have a decided tendency to "ball up" or segregate, and it is not unlikely that some of the duplex inclusions which showed a pale gray center with a yellow rim had originally a eutectic structure.

Röhl's diagram does not account for changes subsequent to

solidification of the sulphides; unmistakable evidences of such changes were, however, observed by the writer. These latter observations appear to be verified by a recent paper on the FeS-MnS system by Zen'ichi Shibata (48) to which the writer unfortunately had no access. An abstract of the paper as prepared by Dr. Kotara Honda reads as follows:

"By means of thermal analyses and microscopic investigation, the author determined the equilibrium diagram of the system FeS-MnS. He found the following facts:

- (1) The melting point of FeS is 1163 ± 2 degrees Cent.; and of MnS 1610 ± 3 degrees Cent.
- (2) The author could not confirm the existence of a compound $\text{Fe}_3\text{Mn}_2\text{S}_7$ found by Röhl.
- (3) FeS and MnS form limited solid solutions alpha and beta with each other.
- (4) Alpha solid solution dissolves 2 per cent MnS at the eutectic point, but almost none at room temperature. On the other hand, beta solid solution dissolves 75 per cent of FeS at the eutectic point, but only 24 per cent at room temperature."

The Reversibility of the Reaction $\text{FeS} + \text{Mn} = \text{MnS} + \text{Fe}$ appears to be established without reasonable doubt. The melts of the author were prepared in vacuo and no oxygen or oxide which is held to be responsible for the "apparent" reversibility of the reaction was present in them. None the less it proved impossible, except in the presence of a most drastic excess of manganese, to obtain inclusions entirely free from the yellow sulphide. The amount of the yellow sulphide was, further, distinctly governed by the amount of manganese present. In other words, a definite equilibrium between the iron, the manganese and the sulphides does exist in the melt. This shows that the reaction is a balanced one, and this in turn implies that MnS must, to a certain extent, be soluble in molten iron. For, FeS and manganese are known to be soluble in iron; hence MnS must be present in solution if it influences the equilibrium. The extent of this solubility is of course very small, as is well known.

5. Summary

The outstanding facts about sulphide inclusions may be summarized as follows:

I. Sources. Sulphides form in the presence of sulphur which

is introduced into the metal primarily with the pig iron and the scrap. Producer gas is also a source of sulphur. (51-52).

II. Formation and Constitution. Iron sulphide is soluble in all proportions in molten iron and essentially insoluble in solid iron. It forms a eutectic with iron of a composition 85 per cent FeS, 15 per cent iron.

Solidification of sulphide-bearing iron will, therefore, take place as follows:

- (a) Pure iron dendrites form and grow
- (b) The remaining liquid surrounding the dendrites becomes richer and richer in sulphide
- (c) This liquid finally attains the eutectic composition and solidifies (at about 980 degrees Cent.) in the dendritic fillings, yielding the cell wall or enveloping membrane type of sulphide inclusions. These inclusions appear to be pure FeS, the eutectic proportion of iron uniting with the neighboring iron.
- (d) Such sulphide as was retained in solution by the solidifying "pure" iron will be precipitated on further cooling. Such precipitated sulphide will appear in the form of very fine globules.

Pure iron sulphide generally forms only in the absence of other sulphide-forming elements, although individual pure FeS inclusions will be found even in the presence of such elements.

In the presence of manganese a considerable proportion of sulphide is converted (in the liquid melt) into manganese sulphide, or rather a solution of iron sulphide and manganese sulphide, the composition of which is a function of the relative concentration of manganese.

Manganese sulphide and mixed sulphide rich in MnS is practically insoluble in liquid iron and will, therefore, crystallize out and float to the top of the melt if opportunity for this be given. Pure MnS can form only in the presence of a considerable excess of manganese and inclusions of pure MnS only when the latter was prevented from reaching the slag.

The solubility in iron of the remaining sulphide is a function of the FeS content of the sulphide. The higher the FeS content the more sulphide is held in solution at a given temperature and the greater is the depression in the solidification temperature of the

iron caused by such dissolved sulphide. In the presence of sufficient manganese some sulphide relatively rich in manganese will crystallize simultaneously with the first iron to crystallize forming a very fine aggregate of globular inclusions. The remaining melt will have a slightly higher relative concentration of FeS and will hence solidify at a slightly lower temperature—solidification of the metal again being accompanied by solidification of sulphide of a corresponding solidification point. Progressively crystallizing portions of the metal become thus richer and richer in relative FeS content (poorer in relative MnS content) and embrace inclusions correspondingly richer in FeS.

As the FeS content of the inclusions rises, the globules at first, become larger and then elongate into streaks. The last sulphide portions to solidify are squeezed into the dendritic fillings, and appear as cell walls just as in the case of pure FeS. These cell walls are made up here, of an aggregate of pure FeS and a limiting solid solution of FeS in MnS.

The globular inclusions are composed for the most part of solid solutions of FeS in MnS, although aggregates of pure FeS and the limiting FeS-MnS solid solution are not uncommon. Pure FeS globules are of course also met with.

In general, in the presence of a sulphide-forming element soluble in iron, sulphides of this element will form at the expense of iron sulphide, to an extent governed by the equilibrium conditions existing in the metal bath. If a sulphide thus formed is largely insoluble in the molten metal and opportunity is given for it to leave the bath, desulphurization (or at least partial desulphurization) of the bath will take place. Such sulphide as remains in solution will, in general, be precipitated on solidification of the iron, the constitution of individual inclusions, their form and location, depending on the temperature and conditions of their formation.

The higher the solidification point of these sulphides the smaller they will, in general, be and the more uniformly distributed. Sulphides which accumulate in solution in portions of the iron last to solidify will be squeezed in the inter-dendritic spaces and solidify there in the form of more or less continuous membranes.

Sulphides precipitated prior to solidification of the metal may be retained as inclusions if they are unable to reach the slag.

III. Behavior. Ordinary heat treatment does not affect the location and form of sulphide inclusions. Migration of sulphides—to grain boundaries (or otherwise)—does not take place, many statements to this effect notwithstanding. Changes within individual inclusions do, however, take place, especially in case of duplex inclusions, where quenching, for example, may suppress the formation of a well developed eutectic, prolonged annealing result in a divorce of the constituents of the eutectic, etc. Sulphide inclusions are plastic at rolling temperatures and are elongated by hot working into streaks.

IV. Appearance. Pure iron sulphide may be described as having a pale “creamy yellow” color. It is distinctly yellowish and differs in this respect from all other inclusions found in iron.

The solid solutions of FeS in MnS have a distinct dove gray color which is generally the darker, the higher the proportion of MnS. The limiting solution of FeS in MnS is of a very pale gray color; the brilliancy of this latter solution is identical with that of pure FeS.

Pure MnS inclusions exhibit ordinarily distinct skeleton crystal outlines.

Solid solutions rich in MnS appear in the cast metal in the form of very fine globules, generally of the order of 0.002 millimeters and less. Solid solutions rich in FeS yield larger globules and elongated forms. Pure FeS appears both in the form of cell walls—often exceedingly fine—and in the form of globules.

V. Reactions. Etching in 10 per cent nitric acid leaves sulphides unchanged.

A 10 per cent chromic acid solution in water attacks MnS and solid solutions rich in MnS; fails however to effect any changes in the solid solutions poor in MnS, especially the limiting solution, and of course in FeS.

Sulphur printing for 20 seconds, using 2 per cent H_2SO_4 , destroys all inclusions containing MnS in solution, and leaves FeS inclusions essentially unchanged. (A stronger H_2SO_4 solution—10 per cent for example—or repeated applications of a 4 per cent solution, destroys FeS).

Boiling sodium picrate blackens all sulphide inclusions.

CHAPTER IV

OXIDE-SULPHIDE INCLUSIONS

WE FOUND that pure iron oxide and pure iron sulphide inclusions can exist only in pure iron, and that in general, in the presence of other metallic elements, oxides, resp. sulphides, of these elements will form, and associate with the oxides, resp. sulphides, of iron in a manner governed by the chemical relationships existing between the compounds involved.

Next the question arises what will happen when oxides and sulphides both are present in the melt, as is, in fact, the case in actual iron and steel-making practice. Will the oxides react with the sulphides as they do, for example, in reverberatory copper smelting, and eliminate each other thereby,



or they will associate peacefully, in a manner analogous to that of oxides among themselves or sulphides among themselves?

1. The Literature on Oxide-Sulphide Inclusions

The literature on oxide-sulphide inclusions is exceedingly meager. Le Chatelier and Ziegler (16) were, it appears, the first to discover, in 1902, the existence of a eutectic between iron oxide and iron sulphide. Examining with the microscope artificially prepared iron sulphide, they noted that "between the yellow grains, and frequently around the grains of iron, a substance is found made up of very fine plates having the characteristic appearance of eutectic alloys or of pearlite. One of the components of this eutectic is the yellow sulphide, while the other is a gray substance whose color recalls the appearance of slag frequently found in iron and steel."

Later writers when mentioning the iron oxide—iron sulphide eutectic refer frequently to the paper of Treitschke and Tammann (23). This, however, contains merely a note calling attention to the findings of Le Chatelier and Ziegler.

Matveieff (54), in 1920, extended his studies of artificial inclusions to the case of mixed oxide-sulphides. He found that there resulted, in general, three constituents:—a mixed sulphide (with

some dissolved oxide), a mixed oxide (with some dissolved sulphide), and a eutectic of the two.

In the chemical literature exist numerous papers on oxide-sulphide relationships; most of them deal only with reactions at relatively low temperatures. Of some interest is a paper by D. L. Hammick (55) describing the action of SO_2 on FeO and on MnO at elevated temperatures. Textbooks on metallography disregard the oxide-sulphide inclusion relationships entirely.

2. Experimental Material

A systematic and thorough study of the more common oxide-sulphide inclusions would imply, first of all, a study of the equilibrium relations of the two fundamental systems:

- (1) Fe-FeO-FeS
- (2) Mn-MnO-MnS

This was not attempted by the author. His aim was rather to gather such general information about sulphide-oxide inclusions as could conveniently be obtained from photomicrographic studies of suitable melts, and to observe to what extent sulphur elimination was assisted by the presence of oxygen.

Two melts only were prepared; the first to show the relationships between iron oxide and iron sulphide in the absence of foreign elements, notably manganese; the second, to show these relations in the presence of manganese.

Melt SO-1

Charge: Sulphide melt S-3 63.0 grams
 Fe_2O_3 2.0 grams
 Melted in air; all the oxide charged into a closed container.

Melt SO-2

Charge: Sulphide melt S-7 22.65 grams
 Mixed $\text{Fe}_2\text{O}_3 + \text{Mn}_2\text{O}_3$ about 1.5 grams
 Melted in air; the oxide charged in the form of pellets dropped in the melt after fusion of the latter.

Known FeS and FeS-MnS -bearing melts were used as a base to which oxide was added. A comparison of the structures with

and without oxide of alloys containing the same (or nearly the same) amount of sulphur was thus made possible. Additional material for the study of oxide-sulphide relationships was provided by the heat treated²⁸ portions of the sulphide melts S-1 and S-6, which will be referred to as S-1Q, S-1A, S-6Q and S-6A, the letters Q and A standing for "quenched" and "annealed" respectively.

S-1Q Bottom part of the longitudinally cut half of S-1 (See Fig. 50). Annealed for 1 hour at 1760 degrees Fahr. (960 degrees Cent.), heated to 1815 degrees Fahr. (990 degrees Cent.) and quenched in ice-brine.

S-1A Top part of the longitudinally cut half of S-1 (See Fig. 50). Annealed for 2 hours at 1760 degrees Fahr. (960 degrees Cent.) and slowly cooled in the furnace.

S-6Q Middle portion of the longitudinally cut half of S-6. Annealed for 2 hours at 1795 degrees Fahr. (980 degrees Cent.), heated to 1830 degrees Fahr. (1000 degrees Cent.) and quenched in ice-brine.

S-6A The other half of the middle portion of S-6. Treated as S-6Q and reannealed by heating slowly to 1780 degrees Fahr. (970 degrees Cent.) and cooling with the furnace.

3. *Oxide-Sulphide Relationships in Pure Iron*

Pure Iron-Oxide-Sulphide Melt (SO-1). This melt, as just pointed out, was prepared by remelting the sulphide melt S-3 with iron oxide.

General Description of the Inclusions. The inclusions in S-3 are shown in Fig. 56, those in SO-1 in Fig. 87. The inclusions in SO-1 appear to be somewhat larger than those of S-3 and, also, decidedly darker. Upon superficial examination one would be tempted to describe them as gray, although, on closer study, they are seen to exhibit a distinctly yellowish tint. At higher magnifications ($\times 500$) the duplex structure of the larger inclusions, and

²⁸Heat treatment was conducted in an ordinary Hoskins annealing furnace and implied the usual amount of surface oxidation.

the presence of a host of minute inclusions, (0.002 millimeters in diameter and smaller), becomes apparent.

Details of the Inclusions. The details of the inclusions (depicted in Figs. 88-92, 93-96) are revealed only at the highest magnifications. Such magnifications show that practically all inclusions are made up of two constituents which are generally associated in a manner typical for a eutectic. One of these constituents is of a yellowish color suggestive of FeS, the other of a gray color suggestive of FeO.

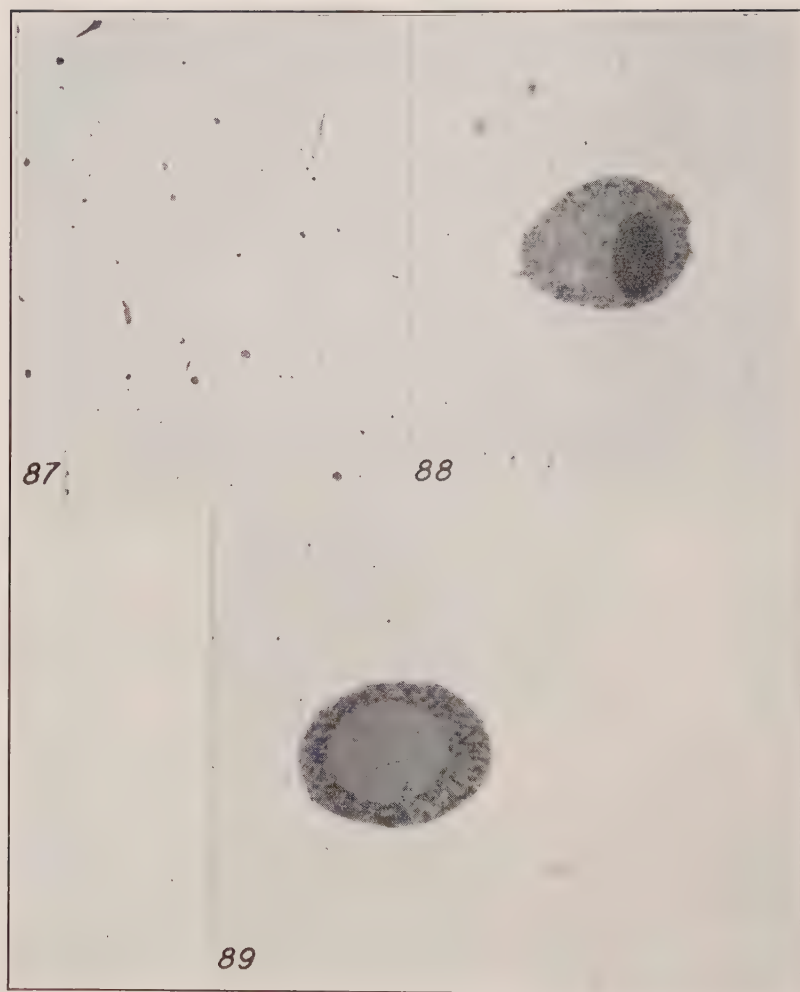
Figs. 88 and 89 are typical for the majority of the inclusions. We have here a well defined (although fine) eutectic surrounding the excess constituent which is either the oxide (Fig. 88), or the sulphide (Fig. 89). Occasionally the excess constituent is seen to be preserved in its original (?) dendritic form as is, for example, the excess oxide of Fig. 90 (large inclusion).

A unique case where all of the oxide appears in the form of dendrites embedded in a sulphide (or submicroscopic sulphide-oxide) matrix is illustrated by Fig 91.

Another unusual case is shown in Fig. 92. Here the oxide and the submicroscopic sulphide-oxide eutectic are arranged in a Widmanstätten pattern which would indicate separation of the oxide from a solid solution.

Considerably more frequent are the structures illustrated in Figs. 93-96. Here, for the first time, we meet a third constituent which appears in symmetrically arranged plate-like forms of a dark gray color. This constituent comes in as an independent unit which, seemingly, does not interfere with the usual FeO-FeS relationship. The early formation of this constituent is suggested by the manner in which the plates, at times, project beyond the general boundary of the inclusions.

What is the nature of this third constituent? It surely is not a sulphide of iron judging by its color; nor is it likely that it is a solid solution of sulphide and oxide, because a solid solution would not crystallize earlier than the pure components. There remains one possibility: the constituent is an oxide of iron different from FeO. May it not be the magnetic oxide Fe_3O_4 ? This oxide is known to occur in solution in FeO. It also appears reasonable to expect that its solubility in FeO which is contaminated by FeS is lower than in pure FeO, and that, therefore, precipitation of



Inclusions in the Pure Iron-Oxide-Sulphide Melt SO-1. Fig. 87—A Group Typical for the Specimen. $\times 100$. Fig. 88—Excess Oxide Surrounded by the FeS-FeO Eutectic. $\times 2500$. Fig. 89—Excess Sulphide Surrounded by the FeS-FeO Eutectic. $\times 2500$.

Fe_3O_4 takes place at an early stage in the history of the solidification of the sulphide-oxide globule.

Let us now examine the evidence furnished by the heat treated sulphide specimens.

The Oxidized Portions of S-1 (S-1Q and S-1A)

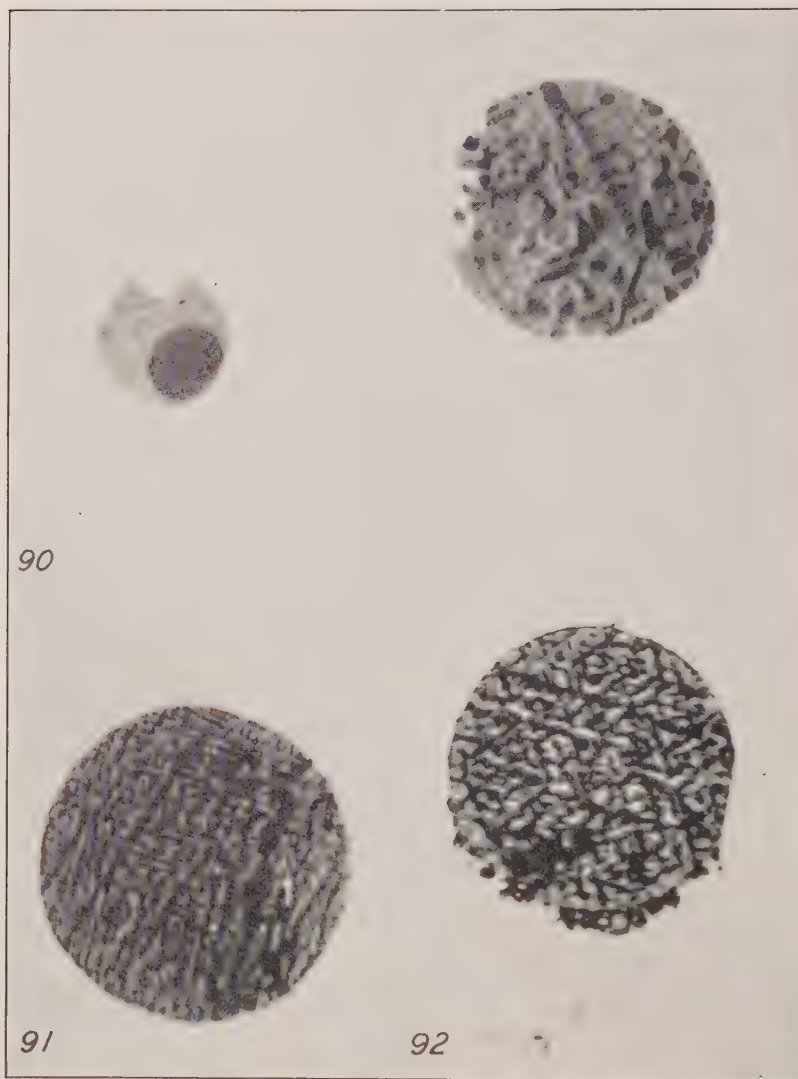
The Mechanism of Oxide Penetration. Previously uniform

sulphide inclusions were found, after heat treatment of the specimens to exhibit a duplex structure. This structure was especially pronounced near the surface of the specimen and became less and less prominent toward the interior. The duplex structure, obviously, was caused by iron oxide which formed on the surface of the heated specimen and penetrated, somehow, to a considerable distance below the surface. Oxidation attendant to ordinary annealing operations fails to penetrate to such depths. In the present case, then, the more or less continuous sulphide network must have served to carry the oxide. The absence of oxidation phenomena in many of the small isolated sulphide globules seems to substantiate this inference.

Description of the Oxidized Sulphide Inclusions (S-1A). Fig. 98 illustrates the appearance of the oxidized sulphide cell walls. The structure is typical for a eutectic (or a eutectoid). One of the constituents of the eutectic is, undoubtedly FeS (or the eutectic Fe-FeS), the other FeO. The proportion of the latter (in the eutectic) appears to be, roughly, 30 per cent, that of the former 70 per cent. (See Fig. 104). Associated with the eutectic we find, again, a third constituent, appearing here in the form of idiomorphic crystals, seemingly reposing on top of the structure. (Fig. 98).

The eutectic varies considerably in structure. At times it is exceedingly fine, and at times so coarse as to suggest a complete divorce of the constituents. An interesting instance of this is pictured in Fig. 99. The eutectic structure of the middle inclusion is so fine that it can hardly be perceived at the magnification used, while that of the neighboring inclusions, removed only a few hundredths of a millimeter from the first inclusions, is distinctly coarse. The difference becomes still more apparent when higher magnifications are used. Compare, for example, Fig. 100 and 102, which depict, at $\times 2500$, the middle inclusion of Fig. 99 and an inclusion immediately adjoining it. In one case we have a very fine eutectic, in the other no eutectic at all,—yet, in both cases, the same proportions of FeO and FeS seem to be present.

In both cases we observe also the presence of constituents other than FeS and FeO. In Fig. 100 a “mid-rib” and a few “side-ribs” of the dark oxide are revealed, while Fig. 102 exhibits the same constituent in the form of a perfect crystal suggesting orthorhombic (or perhaps octahedral) symmetry.



Inclusions in the Pure Iron-Oxide-Sulphide Melt SO-1. Fig. 90—An Example of Excess Oxide Occurring in Dendritic Form. $\times 2500$. Fig. 91—An Unusual Inclusion. Oxide Dendrites in a Sulphide Matrix. $\times 2500$. Fig. 92—Oxide and Sulphide in a Widmanstätten Pattern. $\times 2500$.

In Fig. 102, furthermore, a fourth constituent is visible, intermediate in color between FeO and the dark crystal. It appears as an island faintly outlined in the midst of the main FeO area.

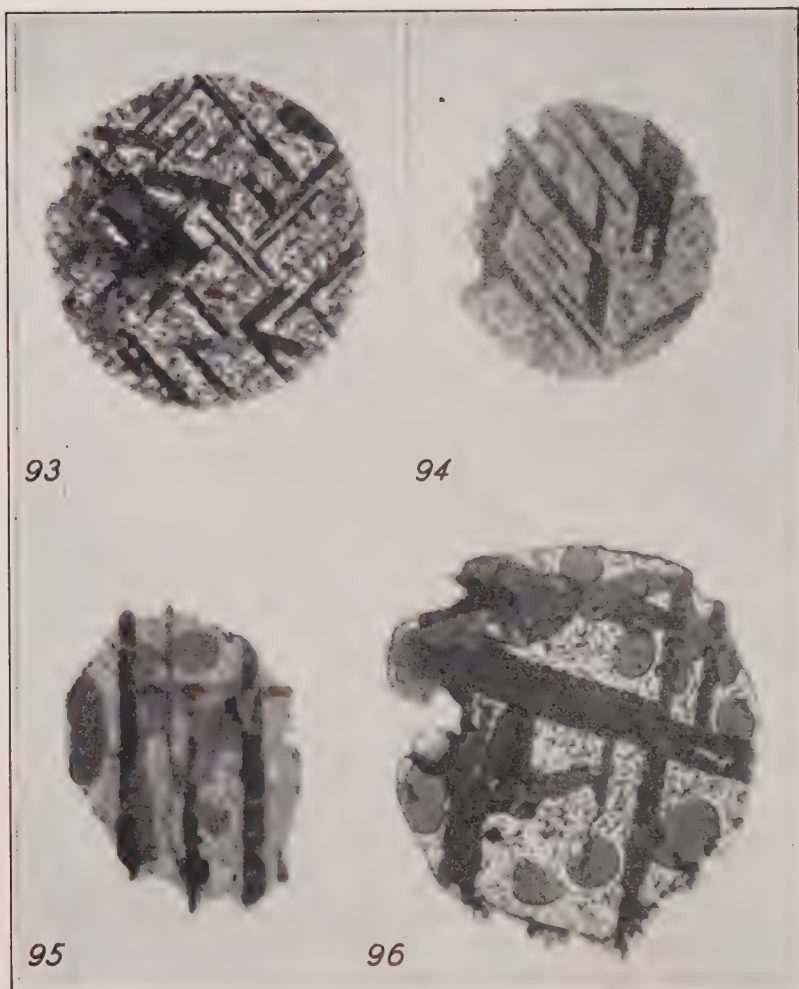
The differences in shade between this constituent and the FeO are so delicate that they are visible only with difficulty even at the highest magnifications used. Once discovered, however, this fourth constituent could easily be found in many inclusions in which it had been previously overlooked. Figs. 101 and 105 serve to illustrate its characteristics. It was found to occur always in close association with FeO, and always in the form of islands surrounded by FeO. The dark crystals, on the other hand, are found to have, at times, an existence independent of FeO. A striking example of this is illustrated by Fig. 103, which shows a dark crystal embedded in faint yellow sulphide.

Etching Tests. Further peculiarities in the oxide-sulphide relationships were revealed on etching for $1\frac{1}{2}$ minutes with a 10 per cent alcoholic solution of nitric acid. This treatment did not affect the dark crystals, nor, of course, the yellow sulphide. The intermediate gray constituents were found, however, to have undergone changes. The boundaries between them, originally faint and indistinct, (perhaps due to the smearing of polishing), appear now clear cut and sharp. The gray constituent enveloped by FeO exhibits, further, signs of having been attacked by the etch. (Figs. 106 and 107). Fig. 107 is of especial interest, showing that even the oxide of the eutectic is complex. Note also the large black crystal in the middle of this inclusion. It crosses sulphide and oxide alike and does not seem to modify in any way the structure of either the complex oxide or the sulphide.

The influence of sulphur printing was studied next. Printing for 30 seconds (using a 2 per cent H_2SO_4 solution) had no influence on the sulphides, induced, however, changes in the oxides which were quite analogous to the changes effected by the nitric acid etch. Prolonged printing developed grain boundaries in the sulphide and caused the complete removal of the darker oxide. (Fig. 108).

The Quenched Specimen (S-1Q). The quenched specimen was exposed to the oxidizing atmosphere of the annealing furnace for a considerably shorter time than the specimen just discussed. Oxidation, therefore, was less pronounced here, and an excess of sulphide, in the oxidized inclusions, was generally noted.

Figs. 109-111 illustrate typical oxidized inclusions of this specimen. The excess sulphide fails, here, to appear in a single area, but assumes a form somewhat suggestive of dendritic crys-



Figs. 93 and 94—Inclusions in Melt SO-1.—Plates of a Darker Constituent (+ FeO) Occurring in Widmanstätten Patterns in the Usual Oxide-Sulphide Matrix. $\times 2500$. Figs. 95 and 96—Inclusions Illustrating the Association of the Dark Oxide with FeO. Note the Manner in Which Some of these Oxide Plates Project Beyond the Main Mass of the Inclusion Causing Reentrant Angles in the Outlines of the Oxide-Sulphide Eutectic. $\times 2500$.

tallization. The eutectic matrix is exceedingly fine—in fact so fine in many instances that the constituents of the eutectic can no longer be seen. The dark crystals are developed just as perfectly as in the previous case (Fig. 111).

Further details about the relationships in quenched sulphide-



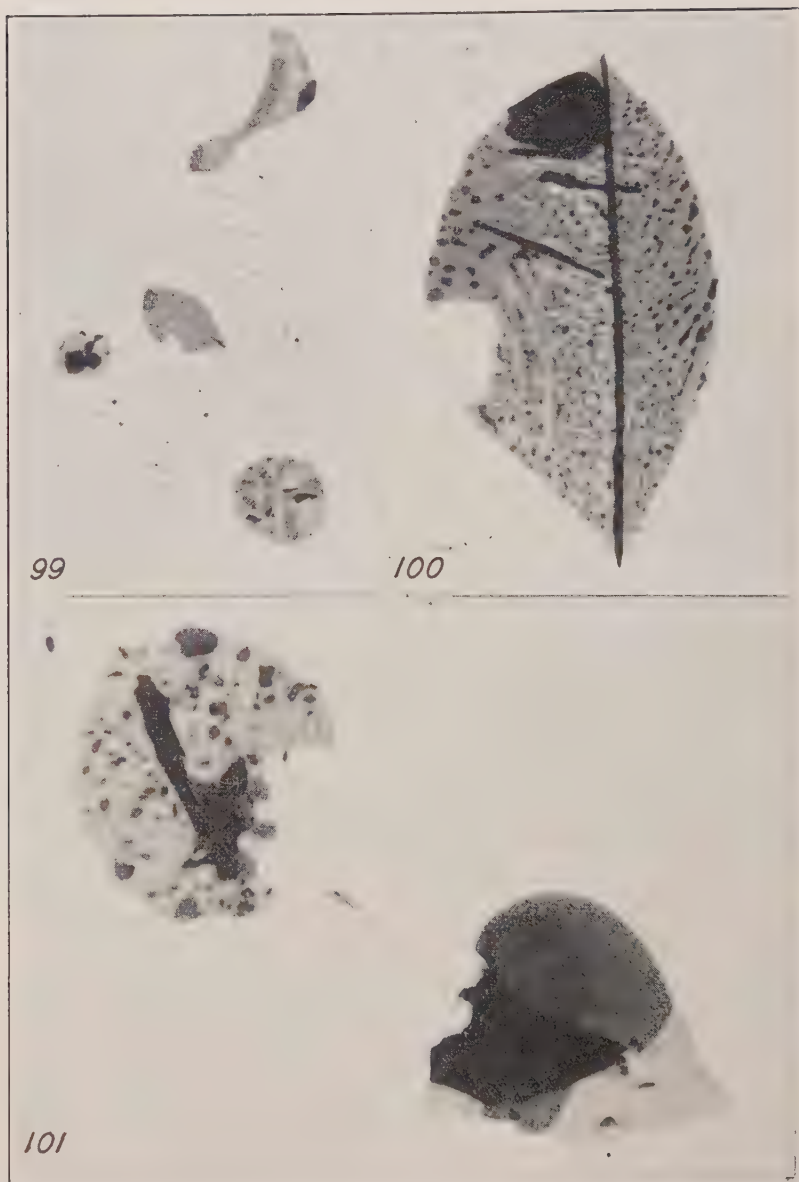
Fig. 97—Melt SO-1—Another Complex Inclusion. Note the Duplex Structure of the Oxide Mass in the Middle of the Inclusion. The Darker Oxide here is Less Dark than in the Previously Described Inclusions—at the Same Time it Fails to Exhibit a Plate Like Form. Note Also the “Balling Up” of Oxide in the Spot at the Right Side of the Inclusion. A “Deoxidized” Sulphide Rim Surrounds this Oxide Globule. $\times 2500$. Fig. 98 S-1A—A Typical Sulphide Stringer Converted to a FeS-FeO Eutectic with two Crystals of a Dark Oxide. $\times 500$.

oxide inclusions (primarily applicable to the case of pure iron oxide and iron sulphide) will be learned from a study of specimen S-6Q.

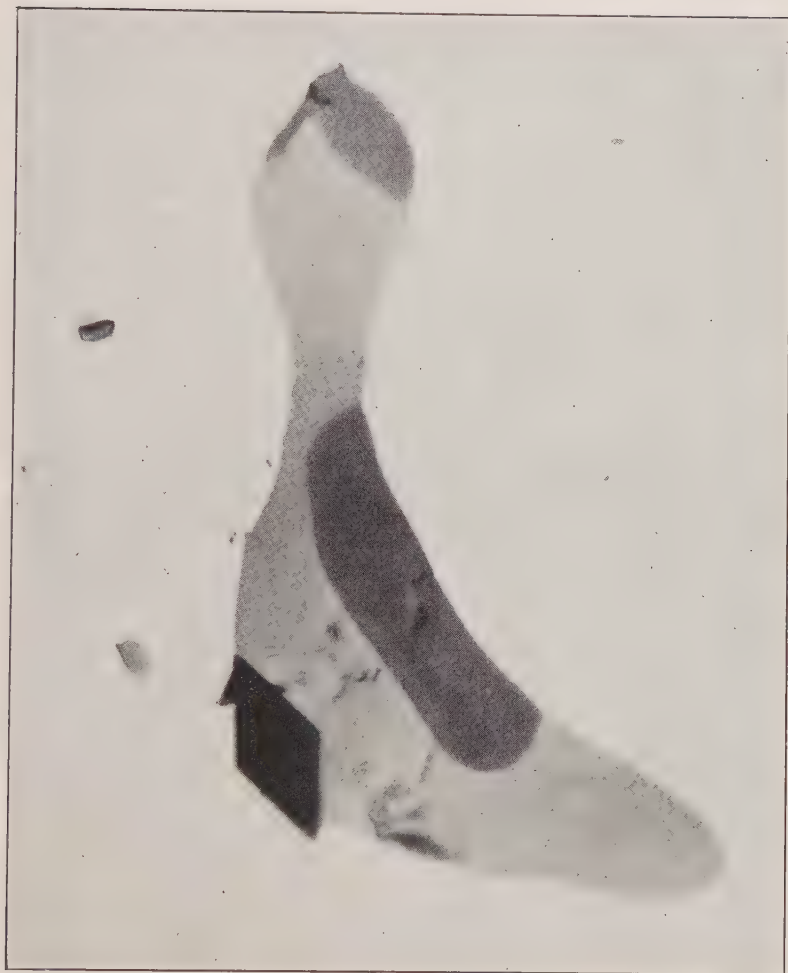
4. *Oxide-Sulphide Relationships in the Presence of Manganese* *The Quenched Oxide-Sulphide of S-6Q*

Description of the Inclusions. Fig. 112 shows a sulphide stringer at the very surface of the specimen, which experienced both thorough oxidation and drastic quenching. Apart from the presence of numerous dark crystals the sulphide appears homogeneous throughout.

There was undoubtedly enough oxide available for the formation of the FeO-FeS eutectic. Its absence, combined with the distinctive mixed yellow gray color of the sulphide, shows that the quenching either prevented separation of the constituents of the



Oxidized Iron Sulphide Inclusions in S-1A. Fig. 99—The Oxide-Sulphide Eutectic Varies Greatly in Fineness in Different, Often Neighboring, Inclusions. $\times 500$. Fig. 100—The Middle Inclusion of Fig. 99 Shows an Especially Fine Eutectic. Note also the Midrib (and Side Ribs) of a Dark Oxide Which Influences the Shape of the Inclusion. $\times 2500$. Fig. 101—The Right Inclusion Shows a Complete Separation of Constituents of Which There are Four: The Crystal, the Dark Oxide, the Normal Oxide and the Pale Yellow Sulphide. $\times 2500$.



Oxidized Iron Sulphide Inclusions in S-1A. Fig. 102—The Upper Inclusion of Fig. 99. Note the Crystal Surrounded by Pure FeS; Also the Dark Oxide within a Patch of Normal Oxide. Complete Separation of All Constituents is Shown. $\times 2500$.

eutectic altogether, or else prevented the separation of constituents sufficiently large to be visible. (Fig. 114).

Alongside of the inclusion just described (Fig. 112) a group of rounded sulphide inclusions rich in MnS is seen. No change, (from the original), in color nor form is discernible in these inclusions. They are either immune to oxide attack at 1795 degrees Fahr. (980 degrees Cent.), or, being discontinuous, they were not

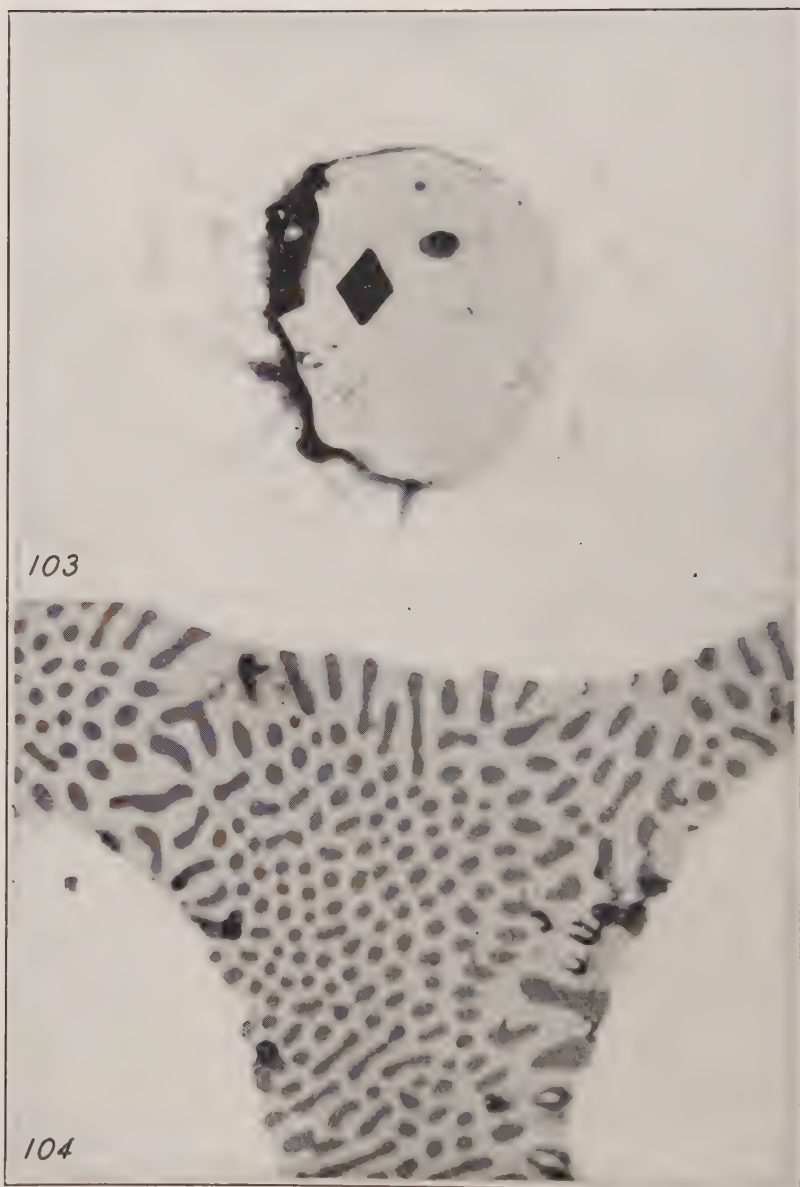


Fig. 103 S-A—A Yellow FeS Inclusion Carrying a Perfectly Developed Dark Crystal. $\times 2500$. Fig. 104 S-A—Inclusion of FeS-FeO Eutectic. The Proportion of Oxide and Sulphide Appears Constant. $\times 2500$.



Fig. 105 S-1A—Three Different Gray Oxides (or Oxide-Sulphides) in a Pure FeS Matrix. \times 2500. Fig. 106—Same as Fig. 105 After Etching for $1\frac{1}{2}$ Minutes in 10 Per Cent Alcoholic Nitric Acid. \times 2500.



Fig. 107—Inclusion in S-1A—The Pitting Effect of 10 Per Cent Alcoholic Nitric Acid on the "Darker" Oxide. Etched for $1\frac{1}{2}$ Minutes. $\times 2500$.

reached by the oxide. At any rate, the appearance of these inclusions is uniform throughout the specimen.²⁹

This is not true of the inclusions rich in FeS. As we proceed from the oxidized rim of the specimen toward the interior a duplex structure becomes apparent in these inclusions. Dendritic forms of the gray color of FeO, or, more often, of the pure yellowish of FeS, are seen to appear here and there in the uniformly colored yellowish gray matrix of the inclusions. (Figs. 116 and 117). It appears that these dendrites represent excess oxide, resp. sulphide, the precipitation of which could not be entirely suppressed by quenching which was less drastic than that effected at the rim of the specimen. Higher magnifications support this inference. Fig. 119, for example, shows that wherever separation of excess oxide has taken place, the eutectic nature of the matrix becomes apparent also. This is equally true for the case of excess sulphide, although, here, the eutectic of the ground mass is visible less clearly (Fig. 120).

In general, we are justified in concluding:

- (1) that we have, at 1795-1830 degrees Fahr. (980-1000 degrees Cent.), a uniform solution of oxide in sulphide (or vice versa),
- (2) that this solution (although preserved on very drastic quenching) can be retained at atmospheric temperature only with difficulty and tends to break up into its constituents.

The appearance and distribution of the dark crystals differs in no way from their previously described occurrences. They must have formed at a temperature above 1000 degrees Cent. and must have essentially completed their outlines before the quenching operation.

Etching Effects. The behavior under etching treatment of the uniform yellowish gray oxide-sulphide (solution?) is of interest. Chromic acid failed to induce any changes in this constituent: attacked, however, some of the darker manganese-rich sulphide inclusions, the remainder of which was taken care of, as was to be expected, by 20 seconds sulphur printing.

²⁹An exceptional inclusion consisting of an aggregate of two "grays"—both typical for MnS rich sulphides—is pictured in Fig. 118. It was found well toward the middle of the specimen and illustrates, in all probability, an unusual sulphide relationship caused by quenching. (No traces of oxide could be located in inclusions nearby.)

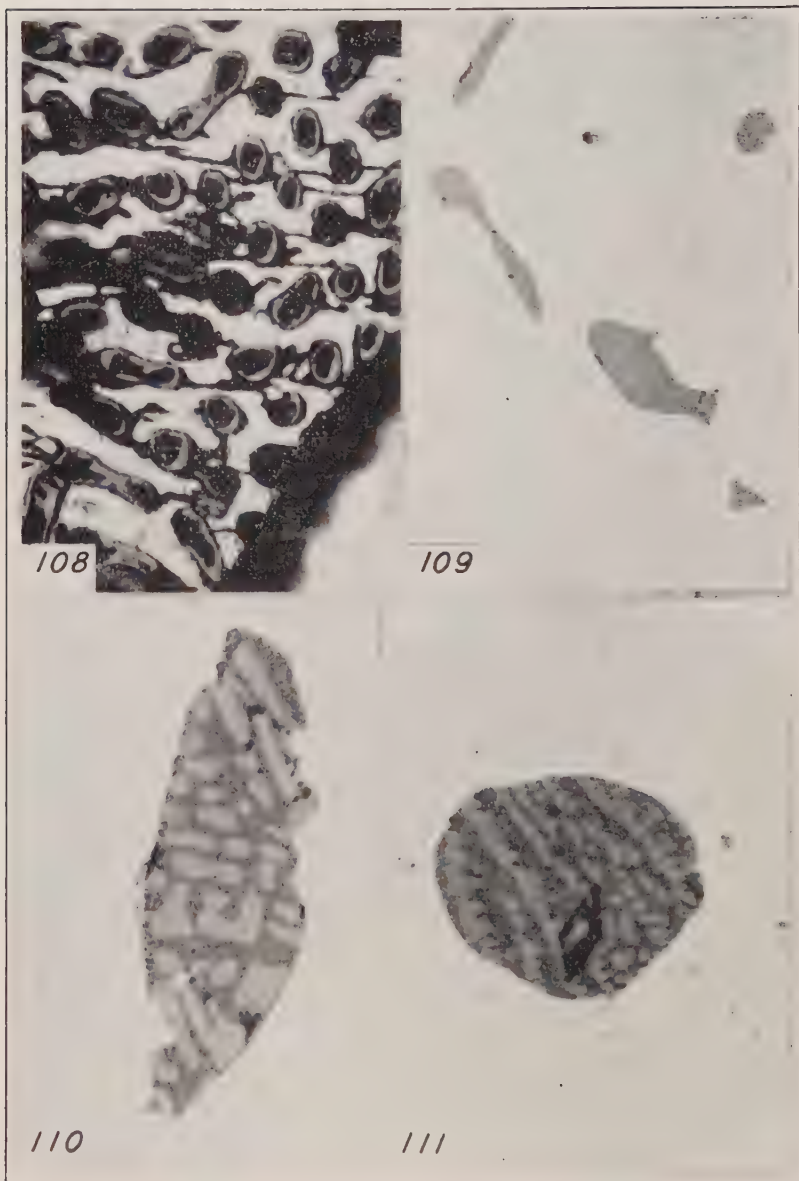


Fig. 108—Inclusions in SO-1—Etching Effects of Sulphur Printing for 3 Minutes. Note the Development of Grain Boundaries in the FeS, the Dissolution of the Darker Oxide, and the Survival of the Normal Oxide Rims. $\times 2500$. Quenched Oxidized Inclusions in S-1Q. Fig. 109—A Faint Duplex Structure is Discernible in Some Inclusions at $\times 500$. Fig. 110—The Excess Sulphide has not had Time to Coagulate. Note the Fineness of the Eutectic of the Ground Mass. $\times 2500$. Fig. 111—The Eutectic of the Ground Mass is not Resolved. Note the Presence of an Oxide (?) Crystal (Which was Pitted Out) in this Inclusion Which Otherwise Suggests the Presence of Excess Sulphide. $\times 2500$.



Quenched Oxidized Inclusions in S-6Q. Fig. 112—Oxidized Sulphide Cell Wall Near the Surface of the Specimen, Drastically Quenched. Note the Absence of a Visible Eutectic in this Yellowish Gray Stringer, Also the Presence of Numerous Crystals. The Small FeS-MnS Dots (Lower Left Corner) Appear Unaffected by the Heat Treatment. $\times 500$. Fig. 113—Same as Fig. 112 After 20 Seconds Sulphur Printing, Using 2 Per Cent Sulphuric Acid. The Crystals are Preserved. Against the Dark Background they Appear now Bright. $\times 500$.



Quenched Oxidized Inclusions in S-6Q. Fig. 114—Middle Portion of Fig. 112. High Powers Reveal a Suggestion of Heterogeneity in the Stringer. $\times 2500$. Fig. 115—Same as Fig. 113 After Prolonged Sulphur Printing. The Crystal Still Present Shows no Signs of Having been Attacked. $\times 2500$.

Sulphur printing had also a disastrous effect on the yellowish gray mixed sulphide. Fig. 113 shows how readily this material was destroyed by a treatment that left both the excess oxide and excess sulphide unchanged.

If the attacked constituent is an aggregate of sulphide and oxide its weakness toward acid reagents can be explained by the fineness of this aggregate. If it is a solution of sulphide and oxide we cannot but conclude that such solutions succumb readily to acid attack. The dark constituent of S-1A showed similar weakness; may it not be a solution of sulphide in oxide after all?

The behavior of the dark crystals is another item of interest. If they are magnetite, as their form and association would tend to suggest, they should be highly resistant to acid reagents. This is precisely what we find to be the case. Ordinary sulphur printing fails to attack these crystals as can be seen from a comparison of Fig. 112 and 113. Even prolonged sulphur printing (for 5 minutes) has no effect on such crystals as are not removed by the dissolution of the matrix in which they are embedded. The crystal preserved in Fig. 115 bears witness to this effect.

Concluding Remark. The features of S-6Q described are concerned primarily with the iron oxide-iron sulphide relationship on quenching. Such inclusions as could be identified as rich in MnS were seen to have remained unaffected by oxidation, and essentially unaffected by quenching. The limiting solution of FeS in MnS, which originally was part of the streaks of predominantly yellow sulphide, is now, undoubtedly part of the solid solution, or of the fine aggregate, into which these streaks were converted. The manner in which this limiting FeS-MnS solution reacted toward the oxide cannot be inferred from the present specimen.

The Annealed Oxide-Sulphide of S-6A

Description of the Inclusions. The structures observed in the quenched specimen were found to have entirely disappeared after annealing. Instead one finds near the oxidized surface the typical oxide-sulphide eutectic, associated with the various rounded MnS-rich inclusions which show no signs of having been oxidized. The amount of oxide diminishes toward the middle of the specimen until, finally, a region entirely unaffected by oxidation is reached. Here the typical sulphide inclusions described previously



Quenched Oxidized Inclusions in S-6Q. Fig. 116—Sulphides Somewhat Removed from the Edge of the Specimen. Hence Quenched Less Drastically. Note the Crystals and the Dendritic Forms of the Excess FeS. $\times 500$. Fig. 117—As Before, with Dendritic Forms of Excess Oxide. $\times 500$. Fig. 118—An Unusual FeS-MnS Inclusion Toward the Middle of the Specimen. (Unoxidized.) It Exhibits Two Different Shades of Gray. $\times 2500$.

are found in precisely the same relationships as before. It was noted, in particular, that the sulphide cell walls were made up, as before, of an aggregate of yellow sulphide and the pale gray limiting solution of FeS in MnS. The appearance of these cell walls after oxidation is depicted in Fig. 121. They are seen to be made up of a eutectic of yellow sulphide and gray oxide.

What happened to the pale gray limiting solution of FeS in MnS which, without doubt, was present in these cell walls prior to oxidation? Is the FeS-MnS solution preserved and represented by part of the gray constituent of the eutectic? Or did the manganese leave the sulphur and join the oxide? Or did the manganese leave the inclusion altogether joining the metal?

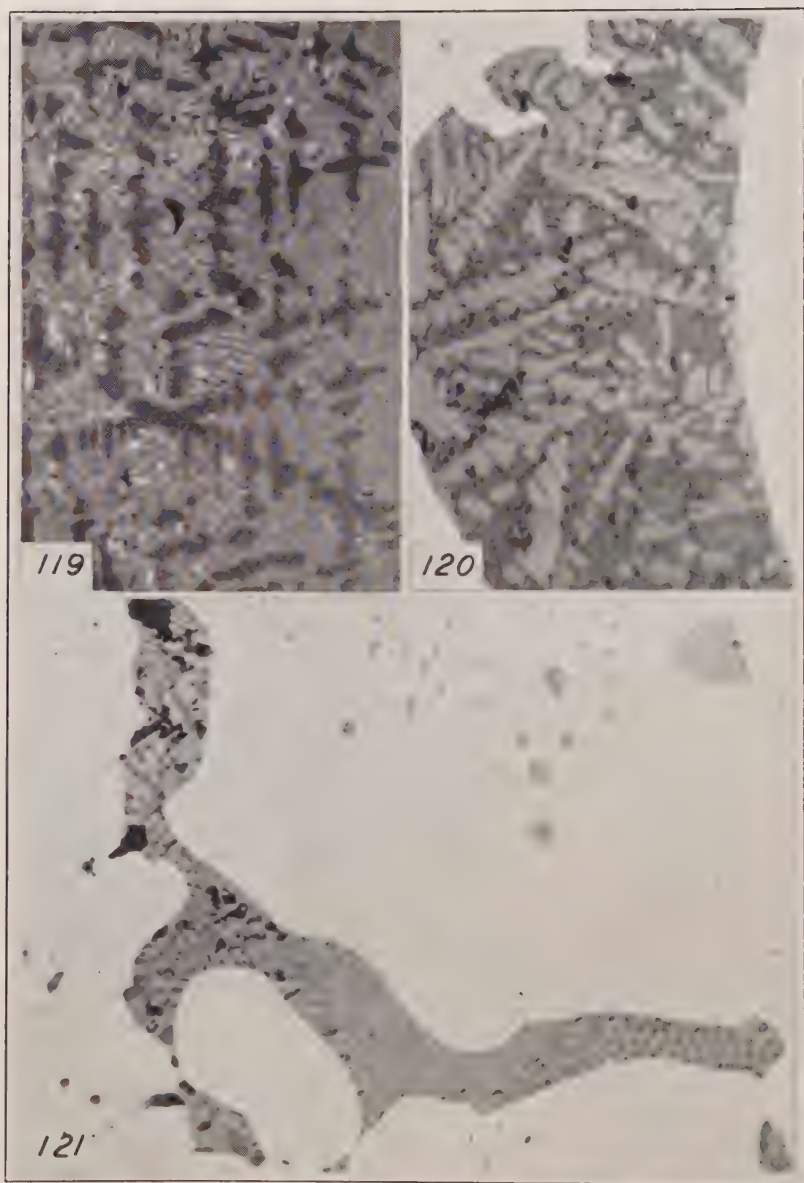
The last suggestion hardly deserves further consideration. The readiness with which manganese combines with sulphur and with oxygen is well known; what could force it to leave these combinations and join the metal? The manganese that was present in the inclusion must, then, be still there.

It is, perhaps, difficult to differentiate between the gray of this sulphide and the gray of the oxide in the eutectic. Still, the difference in shade between the oxide and the MnS-rich rounded inclusions nearby is quite distinct, as is seen from an inspection of Fig. 121. The sulphide appears somewhat lighter than the oxide. The limiting solution of FeS in MnS which is still lighter should, therefore, be distinguishable rather readily from the oxide. A careful search for such lighter specks was made in all of the oxidized inclusions. Only one instance was found where an area of gray, barely lighter than that of the normal oxide, was discernible.

For the general case we must conclude that such manganese as was present in the sulphide cell walls joined, upon partial oxidation of the latter, the oxide portions. This inference is supported by the behavior of these oxide portions toward etching, as will be seen later.

Not all of the oxidized inclusions exhibit the typical eutectic just described. In a number of the smaller inclusions a more or less complete separation of all constituents is observed, much like in the case of some of the inclusions of S-1A. Fig. 122 shows a typical inclusion of this type as recorded through a red color filter. Some five constituents are distinctly visible:

- (1) The dark idiomorphic crystal in the middle,



Quenched Oxidized Inclusions in S-6Q. Fig. 119—Dendritic Forms of Excess Oxide in a Ferritic Matrix. $\times 2500$. Fig. 120—Excess Iron Sulfide in a Ferritic Matrix. $\times 2500$. Oxidized Sulfide Inclusions Quenched and Annealed in S 6A. Fig. 121—The Typical FeS-FeO Eutectic. Note that the Globular FeS-MnS Inclusions (on the Top Middle) Appear Unchanged. $\times 500$.

- (2) A dark gray portion, extending right and left of the crystal, suggestive of manganese-bearing oxide.
- (3) A dove gray area (upper right portion), similar to MnS-rich in FeS.
- (4) A very pale gray spot (upper left portion) such as

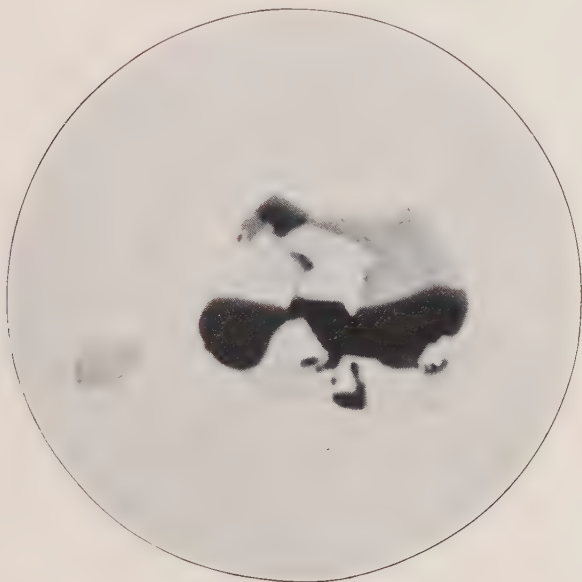


Fig. 122—A Complex Inclusion Showing Complete Separation of Five Different Constituents. Red Filter. $\times 2500$.

exhibited by the limiting solution of FeS in MnS.

- (5) A pale yellow area (lower portion)—FeS proper.

Etching Effects. Etching for 20 seconds by sulphur printing attacked all of the MnS bearing sulphides, and darkened the oxide portions of the eutectic considerably. These oxide portions exhibited, in places, the duplex structure described for S-1A but, on the whole, were found to be more uniform. The oxide in them is of a type rather readily attacked by the acid. This may be caused by the presence of sulphide in solution in the oxide; it is more likely, however, (in the present case), that the presence of MnO in the oxide accounts for it.

Fig. 123 shows the two types of oxide found in the inclusions,—the darker mottled oxide (attacked by sulphur printing)

being the type more frequently represented. This oxide is completely removed on prolonged sulphur printing (2 minutes).

Concluding Remark. The features of the specimen S-6A (and S-6Q) described, do not include the MnO-MnS relationship. The absence, here, of complex MnO-MnS inclusions does not imply that such inclusions cannot exist; it does imply that oxidation at 1795 degrees Fahr. (980 degrees Cent.) in the presence of an excess of FeS, results in the conversion of MnS into MnO which, combined with FeO, makes up the oxide portions of the oxide-sulphide eutectic formed.

What happens at temperatures employed in actual iron and steel making will be shown by the melt SO-2.

The Oxide-Sulphide Melt with Manganese (SO-2)

This melt (SO-2) was prepared by dropping pellets of the mixed oxides of iron and manganese in a remelted portion of S-7 which was originally prepared with the theoretical amount of manganese (to form MnS).

The Effect of Oxide on the Original Inclusions. It will be remembered (see Fig. 81) that a considerable proportion of the S-7 ingot contained dendrites of MnS, while fully 50 per cent of the ingot exhibited the typical clusters of MnS-rich globules. Neither the dendrites, nor the clusters could be found in the melt after the oxide treatment. Instead we have a more or less uniform distribution of fairly coarse rounded inclusions with occasional continuous envelopes (Fig. 124). The majority of the inclusions appear light gray; many are however, distinctly yellowish, suggesting FeS.

Did part of the manganese actually disappear during the melting despite the fact that some was added in the form of oxide, or did the added iron oxide claim some of the manganese from the sulphide? Both possibilities appear to be probable. Preferential oxidation of MnS was indicated already by previously described studies. Discoloration of the crucible walls suggested that they had been attacked by the highly corrosive manganese oxide part of which was thus eliminated from the melt.

Details of the Inclusions. Higher magnification ($\times 500$) shows that about two-thirds of the inclusions are made up of a light gray core surrounded by a shell of a color appearing to be a dark gray.



Fig. 123—S-6A—Portion of a Sulphide-Oxide Stringer After 20 Seconds Sulphur Printing (2 Per Cent Aqueous Sulphuric Acid). Two Oxides Are Present. The Darker One is Pitted by the Treatment. $\times 2500$.

The balance of the inclusions exhibit either a light gray core surrounded by a yellowish envelope, or appear uniformly yellow. These yellow inclusions, at times, show also the dark rim; this is, however, less pronounced than in the case of the gray inclusions.

These relationships are depicted in Fig. 128. The color differences are discernible only with difficulty although a red filter was used in order to emphasize these differences. A careful in-

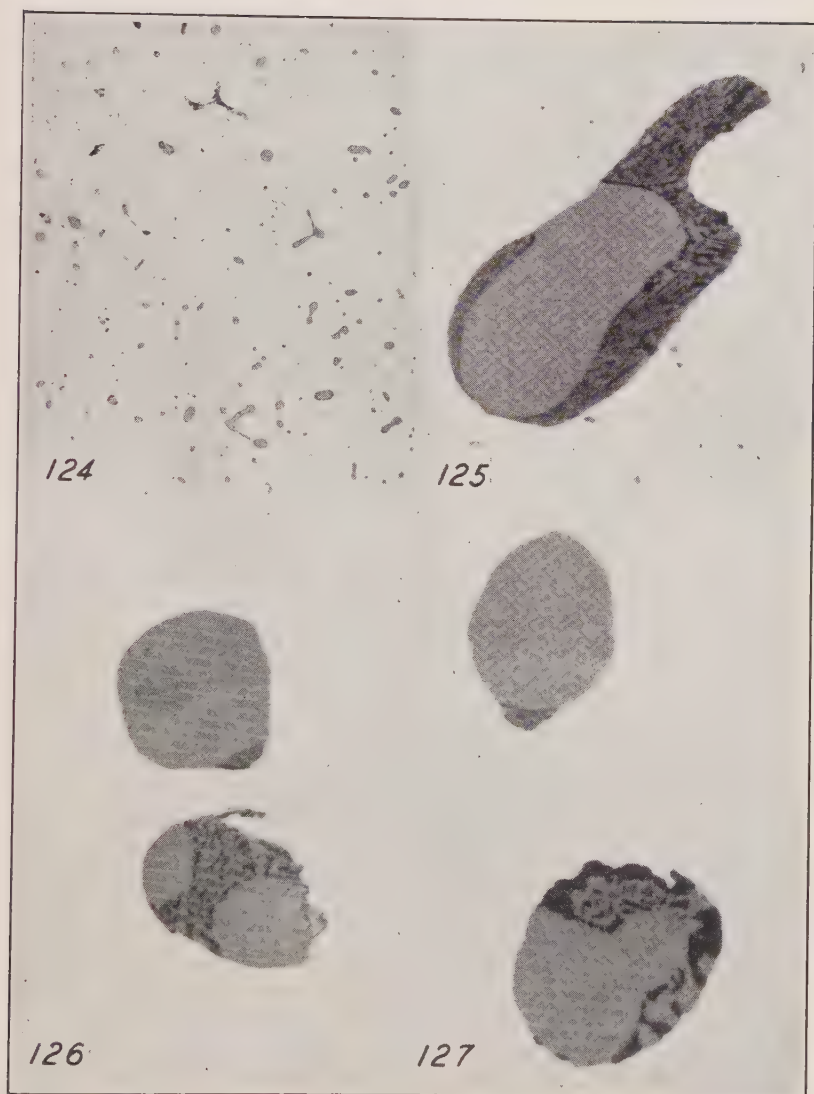
spection of the photograph enables one, nevertheless, to differentiate between the gray (darker) inclusions and the yellow ones (lighter). (The inclusions richer in MnS are further differentiated by etching with chromic acid, as shown in Fig. 129.)

There is no difficulty in observing the dark rims predominantly associated with the gray inclusions. These dark rims, at high magnification ($\times 2500$), are seen to consist of a eutectic of manganese-bearing sulphide and manganese-bearing oxide. That the sulphide contains MnS is obvious from its dove gray color. The oxide, in turn, must be rich in MnO since it displays a color very much darker than iron oxide. The existence of a MnS-MnO eutectic, similar to the FeS-FeO eutectic is thus definitely indicated.

Figs. 125-127 illustrate the occurrence of this eutectic. Fig. 125 depicts a deep gray inclusion with a eutectic of components of the same gray and of a very much darker gray. In Fig. 126 is shown a light gray inclusion associated with the eutectic and immediately above it a yellowish inclusion carrying a faint gray center part. Note the difference in the amount of the eutectic that has developed in the manganese-bearing inclusion and the inclusion practically devoid of manganese. This difference is further emphasized by Fig. 127, showing two neighboring inclusions of which the lower one is gray, the upper one yellow.

It is evident that manganese-bearing sulphides are attacked by oxide more readily than pure iron sulphide. That manganese, in order to join the oxide, actually gives up its union with sulphur, is beautifully shown by inclusions such as depicted in Fig. 130. A gray kernel of a solution of FeS in MnS is seen to be surrounded by a narrow rim of yellow sulphide which, in turn, is surrounded by a eutectic of yellow sulphide and a very dark oxide. This association indicates clearly what happened. The oxide extracted not only all of the manganese from the sulphide portion of the eutectic, it actually claimed some of the manganese from the body of the main inclusion. It is the portion which has "demanganized" in this manner that constitutes the yellowish areas adjoining the eutectic.

The importance of this observation cannot be overlooked. The manganese added to iron or steel acts, first of all, as a deoxidizer, and only such manganese as is in excess of the amount claimed by the oxide becomes available for the sulphur. The beneficial ef-



Iron-Manganese Sulphide-Oxide Inclusions in SO-2. Fig. 124—A Typical Spot at $\times 100$. Fig. 125—A Deep Gray FeS-MnS Inclusion Surrounded by the (FeS-MnS)—(FeO-MnO) Eutectic. $\times 2500$. Fig. 126—Lower Inclusion: FeS-MnS + (FeS-MnS)—(FeO-MnO) Eutectic. Upper Inclusion: FeS with Pale Gray Center Part (Limiting Solution of FeS in MnS) and a Small Amount of a (FeS)—(FeO-MnO) Eutectic. $\times 2500$. Fig. 127—Lower Inclusion: as in Fig. 126. Upper Inclusion: FeS with a Small Amount of (FeS)—(FeO-MnO) Eutectic. $\times 2500$.



Iron Manganese Sulphide-Oxide Inclusions in SO-2. Fig 128—Typical Spot at $\times 500$. Fig. 129—Same After Etching for 10 Minutes with 10 Per Cent Aqueous Chromic Acid. The Gray FeS-MnS Sulphide is Destroyed; the Yellowish FeS and the Dark Gray FeO-MnO is Preserved. $\times 500$. Fig. 130—A Light Gray FeS-MnS Inclusion with a Yellow FeS Rim Surrounded by the (FeS)—(FeO-MnO) Eutectic. The Oxide Extracted Some of the Manganese from the Interior Sulphide Portion. Red Filter. $\times 2500$.

fect on steel of manganese is thus ascribable, primarily, to its de-oxidizing features (and the fact that FeS, in the presence of manganese is not held in solution by solid iron), rather than to its affinity for sulphur and the "harmless" characteristics of its sulphide.

5. *Summary and Conclusion*

We can now summarize the facts about the relationships of oxide and sulphide inclusions as follows:

- I. In the presence of sulphur and oxygen in pure iron, both oxides and sulphides of iron are formed.
- II. These oxides and sulphides form solutions with each other which, on cooling, break up into two major constituents:
 - (1) a constituent which is either mainly iron oxide, or mainly iron sulphide, and
 - (2) a eutectic of these two.
- III. In addition, crystals of magnetite (?) are apt to form, and complex sulphide-oxide solid solutions (or fine aggregates), characterized by their lack of resistance to acid reagents.
- IV. Manganese, if present in small amounts, will combine primarily with the oxygen; the resulting oxide forms a solution with iron oxide and iron sulphide which, on cooling, behaves much like the oxide-sulphide solution of pure iron.
- V. In the presence of considerable manganese, sulphide of manganese will form alongside with the oxide. These (MnS and MnO) form a solution with iron oxide and iron sulphide which solution, on cooling, breaks up into two major constituents:
 - (1) a constituent which is either a solid solution of FeS and MnS , or of MnO and FeO , and
 - (2) a eutectic of these two.
- VI. Complex oxide-sulphide inclusions exhibit varying structures depending on the heat treatment given to the including metal. Quenching, in general, will suppress the formation of the eutectic, and promote fine structures; annealing, on the other hand, promotes coarse structures and a separation of the constituents of the inclusions.

CHAPTER V

GENERAL ASPECTS OF THE INCLUSION PROBLEM

1. Purpose of the Chapter.

STUDIES described in the preceding chapters have dealt with the major class of inclusions:

- (1) The oxides (including silicates).
- (2) The sulphides.
- (3) The oxide-sulphides.

We have studied the details of these inclusions, notably in regard to their appearance, constitution and etching features. At the same time we have endeavored to look into their formation, behavior and peculiarities.

These studies, by necessity, were somewhat confined. They nevertheless warrant³⁰ some generalizations which are of interest and of practical significance. It is the purpose of this chapter to present these general aspects of the inclusion problem, aspects which are to include not only such data as were provided by the present work, but also a brief examination of such theories, hypotheses and recommendations, as have gained widespread recognition and acceptance.

2. What Do We Mean by "Inclusions"

Inclusions have been defined as "substances mechanically entangled by the fused alloy" (50); and as "extraneous bodies held in a metallic mass which remained too short a time in a sufficiently fluid state to allow such inclusions to separate from the mass by reason of difference of density" (57). These definitions are limited; they are, furthermore, encumbered by statements having a bearing on the mechanism of inclusion formation.

More frequently inclusions are classified as "non-metallic or oxidized impurities" in contradistinction to "metallic impurities."

The division of impurities into "metallic" and "non-metal-

³⁰Inclusions present in commercial iron were found by the author to be quite similar to the corresponding types of artificially prepared inclusions.

lic³¹” is hardly descriptive. It is, indeed, strange why carbon or phosphorus, for example, and even “metalloids³²” should be classified as “metallic”, and, on the other hand, why iron sulphide should be termed “non-metallic”. It is further obscure why “non-metallic” should be synonymous with “oxidized”.

The important distinction between “metallic” and “non-metallic or oxidized” impurities lies, [as is pointed out by Dr. Sauveur (58)], in the fact that the first form true alloys with the metal, while the second are associated with the metal in a purely mechanical way. “Alloy-forming” and “mechanically included” impurities would, accordingly, be more descriptive and appropriate terms for these classes.

Inclusions, by general consent, are impurities, i.e., elements or compounds which were not intended nor desired in the metal. They are, further, a special class of impurities, and namely those impurities which are associated mechanically with the metal at ordinary temperatures. A simple yet precise definition of inclusions is, therefore, as follows: “*inclusions or enclosures are impurities mechanically associated with the metal at ordinary temperatures.*”

3. Sources of Inclusion-Forming Materials

Views Generally Held. The principal inclusions encountered in iron and steel are oxides, silicates and sulphides. As a source of these inclusions furnace slag is mentioned most frequently (56, 57). The refractories of the furnace, the ladle lining, the runner brick, are also held to be responsible. Some believe that the reactions which take place in the metal bath and in the ladle are an important source (41, 58, 59).

C. H. Herty, Jr., (61) thinks that there are “five possible sources of non-metallics in open-hearth practice:

- (1) Non-metallic matter in or on the scrap charged.
- (2) Non-metallic matter in the pig iron.
- (3) Non-metallics formed when the pig iron is introduced into the open-hearth by the oxidation of the metalloids (?)³³ silicon, manganese, phosphorus and

³¹This division appears to have been introduced, first, by Heyn (22), p. 71.

³²(58), p. 71.

³³Questioned by the present author.

aluminum, and by the introduction of sulphur from the iron.

- (4) Formation of non-metallic matter when the heat is worked with ore or pig iron.
- (5) Formation of non-metallics when the final additions are made."

It cannot be denied that the original inclusions in the pig iron and scrap may, partly at least, contribute to the inclusions of the metal made from these materials. It appears, however, that inclusions from this source are altogether negligible. Indeed, what can be the significance of a few pounds of oxide inclusions delivered into the bath with the scrap, when tons of iron oxide, each particle of which is a "non-metallic," are charged into the same bath in the form of ore?

The brickwork in and about the furnace is a more serious source but even this source is one of subordinate importance since it yields only accidental inclusions. The same can be said about the slag blanket.

Fundamental Sources. As the author sees it there are but two important fundamental sources of inclusions:

- (1) The oxygen introduced into the metal bath with the ore and from the atmosphere.
- (2) The sulphur introduced with the charge and furnace gases.

In the absence of sulphur and oxygen there could form neither sulphides, nor oxides, nor silicates, and hence there would be no inclusions. It is possible, although, perhaps, not feasible economically, to use materials and a fuel free from sulphur. This would automatically eliminate sulphides.

It is not possible, however, to dispense with the oxygen, since oxidation is the very basis of present methods of iron and steel making, the fundamental mechanism of refining. As long as oxygen is present, iron oxide will be present as well as the oxides of silicon, manganese and other oxide-forming elements. And, consequently, oxide and silicate inclusions will be present. To recapitulate:

Fundamental sources of inclusions are:

- (1) Oxygen } introduced into the metal bath through
- (2) Sulphur } the charge and the furnace atmosphere.

Subordinate sources are:

- (1) The slag in contact with the metal.
- (2) The refractories in and about the furnace.

4. *Status of Inclusions in the Molten Metal and Their Formation*

Knowledge of the ways in which inclusions are formed and of the manner in which they occur in the molten metal is a prerequisite to a rational solution of the problem of inclusion elimination (62, 63). No treatment that can be given to a solid metal is capable of removing the inclusions from it;—this removal has to be accomplished before the metal solidifies.

What is the status of inclusions in the molten metal? Do we have here actual inclusions suspended in the viscous liquid or emulsified in it, or have we but potential inclusions, dissolved in the metal? According to Ziegler (36) the inclusions are not only in solution in the liquid metal but even in solid gamma iron. This view is an extreme one and has not been favored by others. By far the greater number of metallurgists are inclined to believe that inclusions are insoluble even in the liquid metal.

To quote *Giolitti* (57):

“The more persistent, and to us more interesting emulsified sonims are attributed by a very well founded hypothesis to an origin in phenomena similar to those occurring in aqueous suspensions of finely divided bodies, or, more precisely, in true emulsions, formed by minute drops of a more or less viscous liquid suspended in another liquid with which the former cannot mix.”

McCance (41) “is not aware of any facts . . . which would support the suggestion of solubility in steel of inclusions,” and he thinks that “their practical importance is concerned with their existence as suspensions.”

What is the evidence on which the foregoing conclusions are based? Ziegler merely shows that his hypothesis serves to explain many phenomena observed in the crystallization of gamma and alpha iron. His conclusions appear largely unsupported. *Giolitti* does not give the details of his reasons for believing inclusions to be “emulsified”. He points out, however, that the slag blanket

comes into being from reaction products of the charge, globules of slag being formed here and there in the bath and collecting to form the slag. It is entirely feasible, therefore, that portions of "slag" thus formed are emulsified in the boil-period of the charge and are retained by the metal.

McCance assures himself first "that particles of 1/1000 centimeter diameter have practically no chance of reaching the surface" and that, in a typical case the percentage of entrapped particles would be about as follows:

| Diameter of Particles in Centimeters | | Per Cent Entrapped |
|---|----------------------------|-----------------------|
| All over | 3.0×10^{-3} | 0 |
| All over | 2.0×10^{-3} | 54 |
| All over | 1.0×10^{-3} | 88 |
| All under | 0.5×10^{-3} | 100 |

The hypothesis of inclusion suspensions in the liquid metal is, therefore, tenable. McCance, next, shows that a high temperature of casting has been found to promote freedom from inclusions—a fact which can be explained satisfactorily only on the basis of the suspension hypothesis.

Solubility of Inclusions vs. Their Existence as Suspensions

It can hardly be doubted that a considerable proportion of the inclusions found in metals have originated in the manner suggested by Giolitti and McCance. On the other hand, no positive evidence has ever been presented that would refute the existence of potential inclusions in solution in the liquid metal.

The writer has shown, in preceding chapters, that iron oxide and iron sulphide are soluble in molten iron, and that oxides and sulphides contaminated by manganese are also soluble, at least to a certain extent. The solubility of FeO in iron has been demonstrated earlier by Tritton and Hanson (90), and that of FeS by Treitschke and Tammann (23), and Friedrich (50). Theoretical considerations of the equilibrium relations that exist in steel making have been shown to support the contention of a limited solubility in iron of inclusion-forming materials.

Some of the advocates of the suspension theory admit themselves, at times, the solubility of "non-metallics" in liquid iron.

Thus McCance (41) is found to state: "All the evidence is favorable to the view that FeO is in solution in liquid steel." . . . "The more correct explanation of the prevention of sulphur red shortness by manganese is based on the fact that FeS is soluble in liquid steel and separates out as an easily fusible eutectic."

Apparently the suspension mechanism is reserved primarily for silicates and manganese-bearing sulphides and oxides. These are perhaps, the only inclusions likely to occur in ordinary steel; it is equally true that they represent the only compounds for which solubility in steel has not as yet been proved directly.³⁴

The experiments of the author indicate strongly that a considerable proportion of even these inclusions is actually dissolved in liquid iron. It will be remembered that in most of the experimental melts the inclusion-forming material was allowed to fuse quietly inside of an iron container. No agitation, no stirring was resorted to that could have "emulsified" the inclusion-forming material, or have caused its uniform distribution throughout the metal. To the contrary, all facilities were provided for the molten inclusion charge to float bodily to the top of the melt if it desired to do so. And yet no such separation took place except in the case of MnS, and even here it occurred to a limited extent only. Instead we found the mechanically included material to be distributed more or less uniformly throughout the metal—to have dispersed, in fact, instead of agglomerated. What mechanism other than dissolution could have accomplished this?

We must be careful, however, in judging true solubility by the number and size of inclusions found in the specimens referred to. The number and size of inclusions are not necessarily representative of their true solubility. For we may deal here with a diffusion phenomenon which of course implies solubility, but which can effect transfer of material in amounts quite independent of such solubility.

We must, further, bear in mind that the observations just discussed give us no information about the manner in which the inclusion-forming matter is dissolved in the liquid iron. It may well be that ferrous oxide and sulphide are dissolved as such alongside with some silicon, manganese, carbon monoxide, hydrogen, etc., and that they react with some of these latter elements or compounds

³⁴FeO, for example, was held to be insoluble until proof to the contrary was offered.

to form silicates, manganese sulphide, etc., only when the material begins to solidify. It may equally well be that FeO , as such, is not dissolved in iron, but is formed only as a reaction product, on solidification.

It may be argued that the melts of the author were too small to be representative of actual steel-making practice and that conclusions based on the behavior of these melts are, therefore, valueless. Such arguments have been advanced, in the past, on occasions similar to the present one. Their fallacy is obvious.

The size of the melt has nothing whatever to do with the problem. Conditions in which the melting operation was carried out are the only items that count. These conditions were not identical in all respects with those obtaining in practice; nor were they intended to be, inasmuch as it is futile to attempt to solve a complicated problem by involving oneself, at the outset, in a host of unknowns. The conditions were in their essentials, near enough to actual conditions to warrant taking the results as a first approximation to the final answer.

Evidence Furnished by the Size of Inclusions. Giolitti and Tavanti (64), in an attempt to disprove the solubility of inclusions in liquid steel, examined the size of inclusions, first in the metal quenched from the liquid state, and then in the same metal, annealed. They found no difference in the size of a given inclusion before and after annealing. This proves, of course, only that inclusions do not grow on annealing but remain as originally formed. It does not imply that they were insoluble in the liquid metal, for even drastic quenching does not necessarily prevent precipitation from solution.

In the writer's experience the inclusions in rapidly solidified metal are always considerably smaller than those in the same metal, slowly cooled, irrespective of the length of time the metal is kept molten. Does this not imply that growth of inclusions takes place primarily during solidification? And does not this, in turn, suggest that the inclusions, at least partly, are formed only on solidification?

In summarizing the evidence, it appears:

(1) that a considerable proportion of the inclusions found in iron and steel form prior to solidification, existing in the melt as suspensions or emulsions

(2) that an equally (if not more) important proportion is formed only on solidification of the metal, from materials dissolved in the molten metal

(3) that no inclusions of importance are formed after the solidification of the metal.

5. *Conditions Governing the Size, Shape and Distribution of Inclusions*

The size of inclusions of a given kind is governed primarily by conditions imposed upon the melt, after the final chemical reactions have taken place. The longer the melt is allowed to remain liquid, and the higher the temperature at which it is kept liquid the more opportunity is given for suspended immiscible globules to coagulate in the melt and to rise to the surface. The slower the solidification the more perfect will be the segregation into the last portions to solidify of such potential inclusions whose solubility limit is not reached even on manifold increase in concentration. The more pronounced will also be the "mechanical" segregation of such included matter as separates simultaneously with the first crystals of iron. It may be conceived that such matter, provided it remains liquid after separation from the iron, is pushed before the growing crystals of pure iron and brought together to form larger globules or pools. Quick solidification, on the other hand, will prevent both segregation and the mechanical collection of precipitated and suspended matter, which, accordingly, will appear in the form of finer inclusions, more evenly distributed.

The size of different kinds of inclusions, other conditions being equal, will be largely a function of their fluidity at the temperature of solidification of the metallic mass. The higher the fluidity of a given inclusion³⁵ the more readily it will escape from becoming entangled by the pasty iron, and the more readily it will join other inclusions. The reverse will be true of inclusions of high melting point. Their pasty condition will cause them to stick to the iron and stay where they were born. Even if several of such inclusions should meet they will show little, if any, tendency to coagulate. The number of inclusions, other things being equal, varies inverse-

³⁵It must be noted that fluidity is a function of chemical composition, temperature and pressure. Gases liberated in the process of solidification may, locally, cause considerable pressure.

ly as their size, and is, accordingly, governed, for a given amount of inclusion-forming material, by the same conditions that influence the size of inclusions.

The shape of inclusions, in cast metals, is generally spherical unless purely mechanical conditions interfere. Such mechanical conditions are responsible for the network or cell-wall structure exhibited by ferrous sulphide. Indeed, this sulphide is not only soluble in all proportions in liquid iron and is, therefore, easily segregated to the last portions to solidify, it also, (or its eutectic with iron) is characterized by a low melting point and hence great fluidity at temperatures when the iron crystals complete their growth. As a result this sulphide is forced into the interstices between the iron dendrites and is mechanically compelled to occupy the tiny openings in the fillings of the dendrites and the interdendritic boundaries.

While globular forms may be assumed by an inclusion solidifying either before or after the congealing of the metal, crystalline forms constitute, generally, evidence of solidification prior to that of the metal because only inclusions solidifying before the iron will be free to follow their crystallographic habits. Dendritic skeletons, such as were illustrated in Figs. 76-78 and in Fig. 83, are typical for such inclusions.

An inclusion whose melting point lies considerably higher than the temperature prevailing in its immediate neighborhood, at the time of its formation, will of necessity exhibit irregular outlines. The outlines of alumina inclusions depicted on Figs. 31 and 32 are an example.

A somewhat different type of irregularity will characterize "accidental" inclusions, such as are furnished by chips of the brickwork and other refractories which may find their way into the melt. The detailed outlines, here, will ordinarily be fairly smooth due to the partial fusion of the inclusion along the periphery—the shape of the inclusion as a whole will, however, be irregular.

The conclusions set forth above follow from a consideration of simple fundamentals of the physics and chemistry of inclusions. It is surprising, therefore, to find that even about these, apparently so obvious relationships there should be a difference of opinion.

The sulphide network, in particular, has received attention and has been attributed, by many, to a peculiar tendency of iron sul-

phide to "migrate" to "grain boundaries". Expressions like the above appear so universally accepted as representing the facts that a special study of the relationships between the sulphide network and grain boundaries was undertaken. It will be described later. Others have attributed this network to an unusual surface tension possessed by ferrous sulphide. In one case even the "infusibility" of FeS is blamed. To quote Greaves and Wrighton (65): "It (FeS) is very infusible and does not ball up like manganese sulphide—hence is injurious. . . "

Distribution—Minor Segregation. The distribution of inclusions in the metal is influenced by much the same conditions as govern their size and shape. Uniform distribution will be assisted by insolubility and the lack of fluidity of inclusions at the temperature of solidification of the metal, and by quick cooling. Solubility and fluidity, on the other hand, especially when assisted by slow cooling, will favor both the chemical segregation and the mechanical concentration of inclusions toward the peripheral regions of the metal dendrites.

Major Segregation. A systematic study of the distribution of inclusions in commercial ingots has yet to be undertaken. McCance (41) thinks that the ultimate position of inclusions in the ingot "is determined by secondary influences, or the laws of chance." He admits, however, that "some of the worst segregations . . . examined have come from the material between the center and the outside skin." Curiously enough, the present writer observed precisely the same phenomenon in his study of the distribution of inclusions in ingot iron; and found, furthermore, that there exists a distinct parallelism between the distribution of the inclusions and the occurrence of blow holes. This, surely, is not a coincidence, nor are the laws of chance responsible for this. The segregation observed is a direct consequence of the different conditions of cooling and of solidification (and of attendant differences in gas concentrations), prevailing in different parts of the ingot.

The relationships between the size, shape and distribution of inclusions on the one hand, and their relative fluidities, on the other, are admirably illustrated by the complete set of FeS-MnS inclusions that were found to be present in the S-7 melt described. Compare, for example, the inclusions of Figs. 79 and 80. The in-

clusions of Fig. 79 are relatively rich in manganese and possess a melting point only slightly inferior to that of iron. Those of Fig. 80 remained fluid much longer. The former are small, the latter of substantial dimensions. The former, on the whole, are distributed fairly uniformly (see Fig. 81, region in the vicinity of the blow hole), the latter are located primarily in dendritic fillings (bottom regions of Fig. 81). Both are globular except where mechanical forces have come into play. Not so the inclusions of Figs. 76-78 representing crystallization prior to solidification of the metal.

Influence of Working. Hot working, as is well known, deforms such inclusions, as are plastic at the temperatures of working. These inclusions are elongated in the direction of work, the elongation, for a given amount of working, being the more marked the higher the temperature of working, the greater the plasticity of the inclusion at this temperature and the larger the size of the inclusion.

6. Behavior of Inclusions

We have briefly considered the formation of inclusions and have found that all important classes of inclusions come into being and assume an existence independent of the metal shortly after the solidification of the latter.

What is the behavior of inclusions in the solid metal?

- (1) Are they undergoing any changes on annealing, quenching and other heat treatments given to the metal?
- (2) Do such treatments induce inclusions to "migrate" in the metal?
- (3) How does the preferential association of inclusions with ferrite and with cementite come about?

HEAT TREATMENT AND THE STRUCTURE OF INCLUSIONS

The structure of inclusions, especially the complex ones, is, without doubt, affected by heat treatment. This has been demonstrated for the case of sulphide-oxide inclusions (Chapter IV), and there is no reason to believe that other inclusions will behave differently in this respect. Heat treatment affects the structure of all matter, in some cases more, in some less, and inclusions are, of course, no exception to this rule.

Heat Treatment and Changes in Size and Shape of Inclusions

That changes in size and shape of inclusions can be induced by heat treatment, is less obvious.

Opinions of Investigators. Giolitti and Tavanti (64) found that annealing of specimens of steel quenched from the liquid state had no effect on the size of the "slag inclusions" in their specimens; Steinberg (67), on the basis of similar experiments, concluded that inclusions of MnS and FeS grow on annealing.

McCance (68) describes heating a piece of mild steel "which was known to have numerous elongated inclusions" for some hours at 2190 degrees Fahr. (1200 degrees Cent.) and finding "that some of these elongated inclusions had broken up into numerous globules while others were quite intact and were just the same in appearance as prior to the treatment." . . . "This evidently," writes McCance, "was a case of the oxide inclusions going into solution, and subsequently becoming globularized in exactly the same manner as cementite at lower temperatures, while silicate inclusions or slag not being soluble were not affected."

McCance, it appears, did not examine the same spot before and after annealing, and his conclusions are, therefore, open to doubt. In another paper McCance (41) states that on heating sulphide bearing steel above 1795 degrees Fahr. (980 degrees Cent.) "the FeS would redissolve and diffuse into the surrounding steel."

Diffusion in Iron. A priori there is no reason why slight changes in the size and shape of inclusions should not be possible. Transfer of material in solids—segregation or diffusion—is, in fact, known to occur. Such segregation implies a certain solubility in the metal of the segregating element,—the segregation being effected, probably, by successive dissolution and precipitation of this element. Inclusions, generally speaking, are soluble in iron to a very limited extent only, at any rate at the temperatures ordinarily employed in heat treating: we would expect, therefore, segregation phenomena in inclusions to be very slight. And this appears to be the case, since no conclusive proof of such phenomena has ever been presented.

It is of interest, in this connection, to examine the diffusion velocities of some inclusion-forming materials. These diffusion velocities are a measure of the mobility, in the metal, of given constituents and, in a way, a measure of the solubility in the metal of

these constituents. As determined by Ziegler (69) the diffusion velocities for some of the common impurities are as follows:

| Impurity | Speed of diffusion in microns per hour (at about 1300 degrees Cent.) |
|---|---|
| Manganese Sulphide | 3 |
| Mixture of manganese and iron sulphides | 3 to 110 (average 70) |
| Iron sulphide | 140 |
| Carbon (carbide Fe_3C) | 5700 (minimum) 8000 (more representative figure) |

There is no doubt that many of the inclusion-forming compounds can introduce themselves into a solid metal by the process of diffusion, in much the same way as carbon does in cementation. This process, as is obvious from the above figures, is exceedingly slow even at temperatures which, ordinarily, are not employed in heat treating.

It furthermore, must be kept in mind that diffusion, while pronounced in a material free from the diffusing compound, is far less effective in a material already contaminated by that compound. And inclusion-bearing metals not only contain the compounds which are supposed to diffuse in them; these compounds had already all the opportunity to diffuse and to distribute themselves in a preferred way, at temperatures very much more favorable to diffusion than those employed in heat treating.

Reactions between Solids. Attention must also be given to the phenomena of reactions taking place in solids and between solid reagents. Such reactions are described by Tammann (70), Desch (71) and others (72, 73). But again it must be borne in mind that such reactions between solids as are indicated in metals, had ample opportunity to complete themselves at the high temperatures prevailing immediately after solidification, and that little, if any readjustments can be expected to take place at lower temperatures.

Conclusion. While changes in inclusions may be expected to take place on heat treatment, such changes appear, in general, to be entirely insignificant,—unless, indeed, the heat treatment used implies chemical changes. (Cementation, for example will destroy oxide inclusions, oxidation from oxy-sulphides, etc.)

Heat Treatment and "Migration" or Inclusions

If heat treatment is incapable of inducing significant changes

in the immediate neighborhood of an inclusion, how can we expect such treatment to cause the migration of inclusions in the metal? Yet is not precisely this implied by statements often met with in the literature?

The following are but a few examples: R. S. Dean (65) writes:

“ . . . brittleness is greatly accentuated by the presence of considerable sulphur in relation to the manganese and also by annealing under oxidizing conditions, whereby an eutectic of FeS, Fe, FeO is formed which melts nearly 100 degrees below the Fe-FeS eutectic. Finally, by cooling rapidly, the segregation of these materials into the grain boundaries and consequent brittleness, may be prevented . . . The rate of segregation of the impurities into the grain boundaries is important in determining the cooling rate necessary to prevent brittleness. . . ” He, then, lists the diffusion velocities, at 2370 degrees Fahr. (1300 degrees Cent.), for MnS, FeS and Fe_3O_4 (should be FeO), given by Ziegler and concludes: “The difference between the diffusion velocities of MnS and FeS is striking and accounts for the greater slowness with which a high manganese ingot iron may be cooled without inter-crystalline brittleness.”

McCance (41) states that on heating steel above 1795 degrees Fahr. (980 degrees Cent.),—the eutectic temperature of Fe-FeS—“the FeS would redissolve and diffuse into the surrounding steel, and on cooling again below this temperature would not be redeposited in its original position, but would be deposited in between the crystal grains according to its habit.”

G. Röhl (37), referring to the regularity of iron sulphide cell walls, writes: “The prominence of the symmetrical arrangement of the crystalline grains of the iron”³⁶ is remarkable in connection with the higher percentages of iron sulphide.”

Does Iron Sulphide Seek Grain Boundaries? It was conclusively shown in the preceding that the symmetrical arrangement of the sulphide envelopes is ascribable solely to their location in the dendritic fillings and the inter-dendritic spaces. (Chapter III). It was further shown (Chapter III) that ordinary heat treatment does not induce any detectable migration of the sulphide. And why should the sulphide seek to locate itself in the boundaries of the crystalline grains of iron? It does so “according to its habit” writes McCance. Let us examine this habit.

³⁶Röhl refers to his Fig. 2, which is similar to the author's Fig. 43.

Fig. 131, shows an unusually symmetrical group of sulphide cell walls supposedly located on the boundaries of individual iron grains. Yet etching (with 10 per cent HNO_3) indicates that they are located all within one single crystalline grain of iron. Fig. 132 illustrates the uniform attack by the acid of this single grain. This may not appear a satisfactory proof of the homogeneity of crystalline orientation. Let us examine, then, the orientation of the metal as revealed by etching pits visible at high magnifications. Fig. 133 shows them. They are seen to have the same orientation on different sides of the sulphide "boundaries", and, in fact, were observed to have the same orientation throughout the entire area pictured in Fig. 132.

What is the situation at the actual grain boundaries? Examine Fig. 134 which illustrates a typical spot of the sulphide specimen S-1. The actual grain boundaries are seen to be essentially independent of the sulphide stringers. Their details only, are affected by these sulphides. Observe, for example, the offsets in the grain boundary in Fig. 134, in places where it meets and crosses the sulphides. That the outlines of the crystalline grains of iron should be influenced by the preexisting sulphide stringers, to the extent shown, is quite in accord with what we would expect. The existing relationships are further described by Figs. 135 and 136. The manner in which a grain boundary line, bearing a right angle relationship to some sulphide walls, is seen to pass through these sulphides (cracking them locally) is especially interesting (Fig. 135).

A more detailed study of sulphide and grain boundary relationships which was undertaken by the author will not be described here. It served but to substantiate conclusions arrived at from common sense considerations.

The mechanism of sulphide distribution is governed by conditions of solidification of the metal. The number of the crystalline grains of the metal, their size and development, is a function of conditions prevailing subsequent to solidification, more specifically, of conditions below the Ar_3 point. Grain boundaries can be and are influenced by the sulphide only insofar as they interfere, mechanically, with their normal development. Why then the widespread notion of sulphide occurrence at grain boundaries?

The explanation appears simple enough. The first crystalline

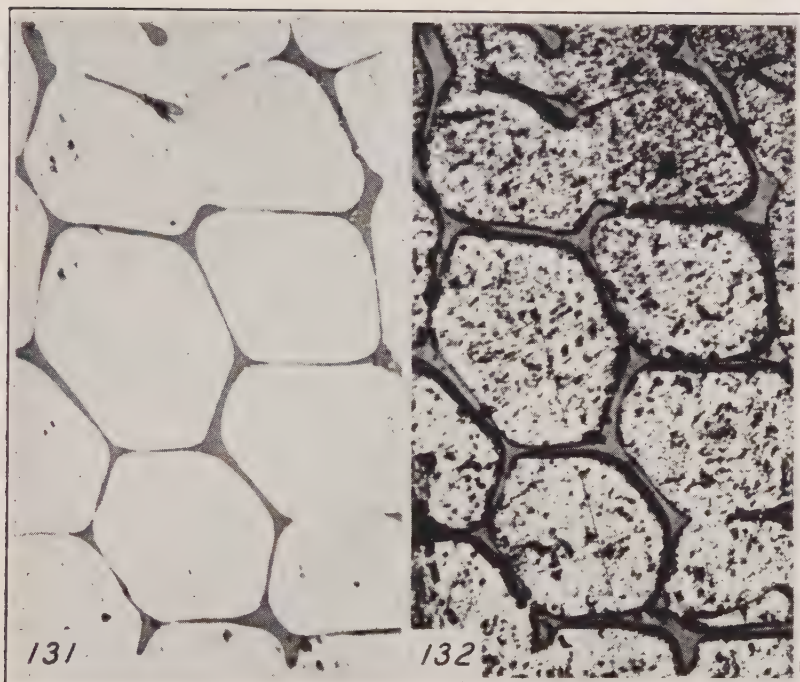


Fig. 131—A Group of Unusually Symmetrical Cell Walls of Iron Sulphide, (in S-1) $\times 300$. Fig. 132—The Same Group After Etching with 10 Per Cent Alcoholic Nitric Acid. The Cells are Located within a Single Crystal Grain of Iron. $\times 300$.

units or grains of a metal are the dendritic grains and it is at the boundaries of these grains, (and in the dendritic fillings), that the sulphide is located. Le Chatelier (16) had these primary grains in mind when he spoke of "a membrane around the crystallized grains of iron." Many later writers, recounting the findings of Le Chatelier and other early investigators, merely mentioned the fact of sulphide occurrence at grain boundaries thinking it superfluous to be more precise and specific.

Now, speaking about the crystalline grains of a metal we have in mind the existing crystalline grains and not the grains that were present in the metal months or, perhaps, years ago. Hence the confusion and the attempts to account for the existence of iron sulphide at "grain boundaries" by some process of migration or diffusion, or by just a mysterious "habit" of FeS . Another item which, undoubtedly, contributed to the confusion is the omission,



Fig. 133—Portions of Three Random Cells of Fig. 132. Etching Pits Prove the Identity in Crystalline Orientation of these Cells. $\times 2500$. Fig. 134—Grain Boundaries Fail to Follow the Sulphide. The Latter Modifies the Details of the Grain Boundaries. Note the Offsets in the Right Boundary. $\times 100$.

already by early writers, of mentioning the dendritic fillings as a place of sulphide occurrence. Many of the regular meshes, outlined by sulphide, are cross sections of dendritic branches and not of the primary grains.

Conclusion

What has been said about the "migratory" habits of iron sulphide applies to other inclusions as well. Even more so, for these other inclusions are all less soluble in iron and diffuse with greater difficulty, with the exception, perhaps, of iron oxide. Inclusions are thus essentially fixed in solid iron and steel. They do not migrate.

The Preferential Association of Inclusions with Ferrite and Cementite

How can we account for the preferential association of inclusions with the ferrite of hypoeutectoid and the cementite of hypereutectoid steels? If the inclusions are fixed it is clearly the ferrite, resp. the cementite, that seek the inclusion bearing portions. Why?

According to M. Ziegler (36) the inclusions serve as nuclei for crystallization, producing an effect on solid solutions analogous to that produced by small particles of foreign matter in the crystallization of salts from liquid solutions. Ziegler thinks that the majority of inclusions are dissolved in solid gamma iron and precipitate on cooling, on the boundaries of the gamma grains producing thus an inclusion network. It is this inclusion network that the ferrite resp. cementite, is precipitated on when the Ar_3 (resp. Acm) point is passed. Hence the association.

H. M. Howe's reaction to this view point is worthy of being quoted in detail. He writes (74): "The common occurrence of slag within ferrite masses . . . is usually supposed to be caused by some attraction which the slag has for the ferrite. But by what piping does this Pied Piper entice the ferrite from within the austenite, draw it across considerable distances, and enwrap itself in it as in a garment? Why create so improbable an explanation when the ejecting power of the austenite would lead to just this stratigraphic occurrence? . . . "Each austenite grain is an organism with the power of expelling foreign matter to its surfaces and to its cleavages." "The austenite grains while above

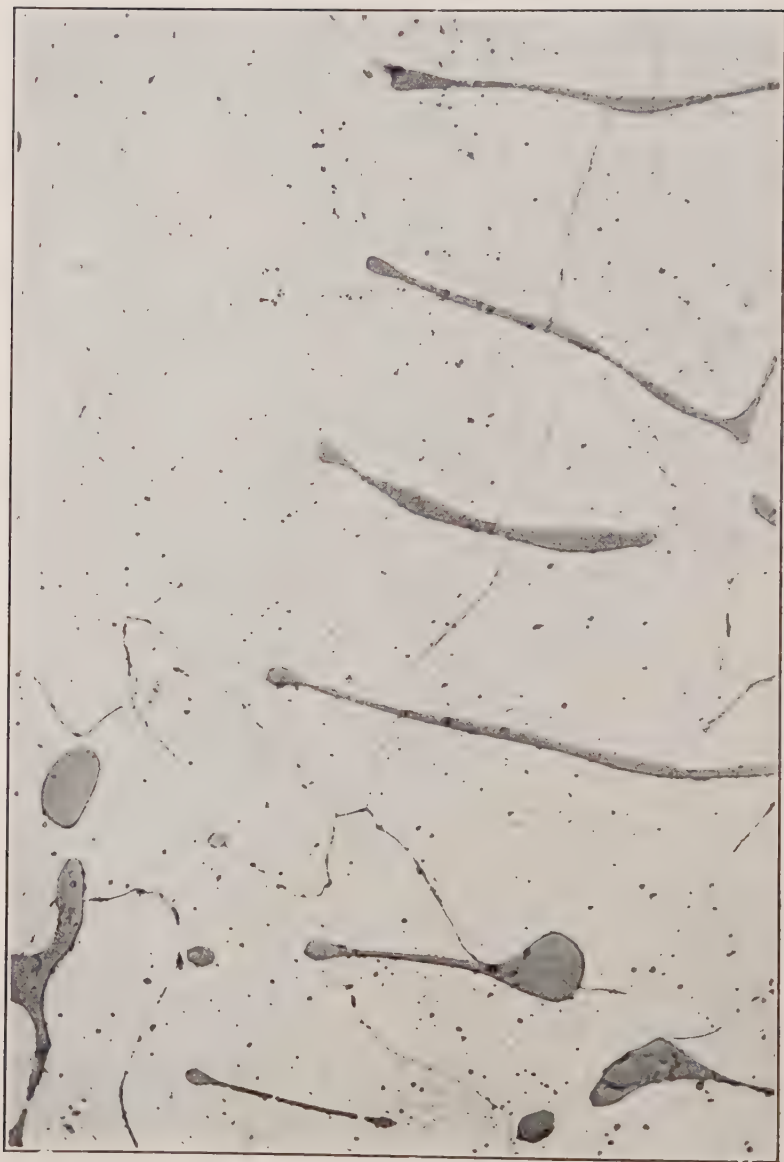


Fig. 135—S-1. Etched with 3 Per Cent Alcoholic Nitric Acid. The Grain Boundary Line is Offset Where it Crosses the Sulphides. Some of the Sulphides Appear to be Cracked Where the Grain Boundary Passes Through Them. $\times 500$.

the transformation range would naturally dispose along their surface or their cleavages any slag which they contain. In later cooling through that range they arrange the proeutectoid element then born in like manner and hence this later arranged matter is found surrounding the earlier arranged slag, which itself is most unlikely to have any such power of arranging its disconnected masses geometrically. Because the crystalline power of the austenite is the only agent which can have arranged the slag thus geometrically, we infer reasonably that it is also the agent which has thus arranged the pro-eutectoid element."

Professor Howe, like Ziegler, holds that inclusions are soluble in the austenite. No experimental evidence has ever been offered for the support of this view. To the contrary, all evidence obtained shows inclusions to be essentially insoluble in solid iron. Apart from this, Professor Howe's hypothesis is open to serious doubt since inclusions are not found to occur in Widmanstätten patterns as is demanded by this hypothesis. Professor Howe is, however, consistent in advocating such an occurrence. If inclusions are soluble in solid iron they should come out of solution in a corresponding manner, i.e., in precisely the same manner as the other pro-eutectoid constituents. Let us be equally consistent.

The position of inclusions in the metal, as we have seen, is governed by the mechanism of solidification of the metal, i.e., by the process of primary or dendritic crystallization. The same or a related mechanism must be responsible, then, for conditions which cause the ferrite, resp. cementite, to appear in association with the inclusions. It is the mechanism of dendritic segregation. This process concentrates the alloy-forming impurities in iron into the dendritic fillings and inter-dendritic spaces, i.e., into places where many (or even most) inclusions also are deposited.

In particular, it is phosphorus which segregates, as has been proved by Stead (25). This phosphorus, as has been shown further by Stead, diffuses only with great difficulty, even at elevated temperatures, and exerts, at the same time, a repelling action on carbon (or on the carbide Fe_3C) which diffuses readily. As a result the carbon is expelled from regions rich in phosphorus, i.e., from the fillings, which are thereby decarbonized or ferritized. Hence the ferrite surrounding the inclusions and the presence of inclusions in the ghost lines of forged steel (76). But what about the preferential association of inclusions with cementite?

The author ventures to suggest that such a preferential as-

sociation does not exist. We took it for granted, heretofore, that inclusions are found primarily in the ferrite, resp. cementite of steel. The basis for this belief is furnished by observations which, in the case of ferrite, are entirely convincing. Not so in the case of the cementite of hypereutectoid steels. Such steels have been studied far less universally than ferrite-bearing steels and the evidence in regard to the occurrence of inclusions in the proeutectoid cementite is inconclusive.

We must bear in mind that, while inclusions can be seen quite readily in the structureless brilliant surface of unetched iron or steel, their presence becomes far less apparent when an etched specimen is examined. Compare, for example, the readiness with which the presence of individual inclusions is called to our attention in Fig. 63 and Fig. 136 which depict entirely comparable inclusion-bearing areas in pure iron before and after etching. How much more obscuring must be the etching effects exhibited by pearlite! Or of any other constituent in which a fine structure is developed. It is only natural that we overlook the inclusions occurring in pearlite, while we cannot help noticing them in the brilliant structureless cementite.

It appears that inclusions may be associated preferentially with proeutectoid cementite only to the extent to which the boundaries of austenite grains are coincident with the boundaries of the primary dendritic crystals, or to the extent to which the development of the austenite grain boundaries has been influenced by pre-existing inclusions. On the whole the existence of a marked preferential association of inclusions with cementite is open to doubt.

In conclusion, it appears desirable to point out that the mechanism of dendritic segregation, although the main cause for the occurrence of inclusions in ferrite areas, may not be the only cause. It is entirely feasible that inclusions, under suitable conditions, may act as nuclei in the process of secondary crystallization of steel (as was suggested by Ziegler), and assist, in this manner, in the accomplishment of a preferential association.

7. *Identification of Inclusions*

It is not the purpose of this chapter to enumerate the methods which have been proposed and used for the identification of inclusions, nor to present a new method. Attention will be devoted, primarily, to some fundamental considerations which ap-

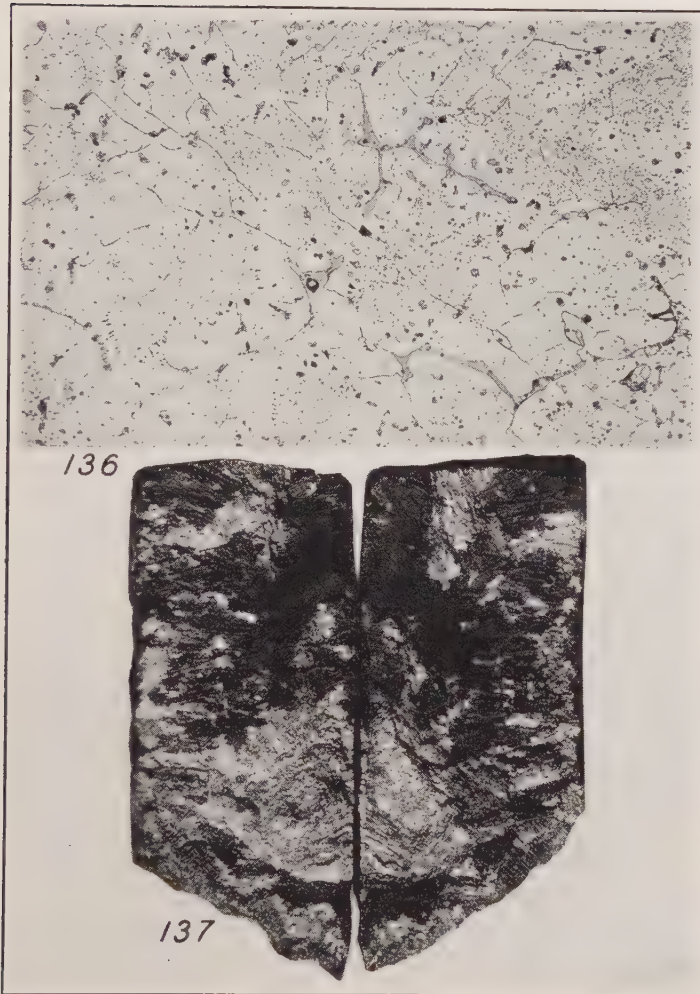


Fig. 136—S-6. Etched with 3 Per Cent Alcoholic Nitric Acid. Grain Boundary Lines are Independent of the Sulphide Inclusions. $\times 100$. Fig. 137—White Cast Iron Exhibiting "Hot Cracks" Broken with a Blow of the Hammer. The Metal Fails Along the Brittle Inter-Dendritic Surfaces of Cementite. $\times 2$.

pear to have received much less attention than they deserve.

It is important, in the first place, to emphasize that the majority of inclusions are not simple compounds as would appear from the "Methods for Identification" proposed. On the contrary,

most inclusions are complex solid solutions or aggregates of such solutions.

Secondly, it is important to note that the methods generally used for the identification of inclusions are not precision methods as one might be led to infer from the way in which directions for their application are given.

Etching Tests. Indeed, all of these methods depend on the application to inclusion-bearing steel of certain etching reagents and a visual judgment of the effect of this reagent. The changes produced by a certain reagent in a given inclusion are not only a function of the chemical composition of the inclusion but a function of the size of the inclusion, the duration of the treatment, of the temperature at which it is carried out, and to an important degree, a function of the chemical character of the surrounding material.

Consider, for example, the effect of the 10 per cent solution of chromic acid in water on manganese-bearing sulphide inclusions. In detail, its effects, as described in Chapter III, were found to be highly variable. Indeed, while it attacked successfully the small globules of manganese-rich sulphide it failed to induce noticeable changes in the larger sulphide inclusions of essentially the same composition. Applied to the specimen S-6 relatively poor in MnS, it exerted a profound attack on inclusions but slightly richer in MnS than the limiting solution of FeS in MnS. In the presence, however, of the other inclusions still richer in MnS—as in S-7—it failed even to tarnish inclusions of the very same composition as it blackened and dissolved in S-6.

Chromic acid is a delicate reagent, highly susceptible to extraneous influences. Other reagents, less delicate and less susceptible, such as sulphuric acid, for example, can almost always be depended upon to produce decisive etching effects. These reagents are, however, so powerful as to be incapable of making fine distinctions. The effect of still other etching reagents will, in general, lie somewhere between these two extremes.

We cannot, then, rely on etching treatments as a precise means for identifying inclusions. The results of such treatments are merely indicative of the constitution of inclusions and must be interpreted in the light of such other evidence as can be secured.

Other Tests. The problem of identifying inclusions is in many

ways comparable to the problem of identifying opaque minerals under the microscope. In this latter case we deal, ordinarily, with much larger masses than are provided by inclusions,—masses which often can be studied in detail already at $\times 100$. Yet the mineragraphist finds it necessary to supplement etching tests by precise measurements of hardness (77), color composition (78), electrical conductivity, etc. .

How can we then hope to obtain reliable results by etching tests alone, while dealing with particles so minute that a magnification of some 1000 is required to study them comfortably? The very minuteness of these inclusions may prevent, of course, the successful application of some of the tests available to the mineragraphist;—at least until special microapparatus is devised for such tests. Other tests, such as a quantitative color test, are quite feasible, however. Chemical methods of testing could also be improved upon materially; using, perhaps, the micro-manipulator of Zeiss, or other devices of the same character.

For general informative purposes we need not go that far, however. The inclusion problem is very much simpler than the corresponding problem of opaque minerals, in one important respect. While the mineragraphist has to differentiate between hundreds of different minerals, the metallographist has to deal with but a few varieties of inclusions. If observations made in one series of tests are checked by those of another series the results, usually, can be taken to represent the facts.

Check Afforded by the Chemical Analysis of the Metal. It is desirable, in all instances, to check one's findings by referring to the data of a careful chemical analysis of the metal. In the essential absence of sulphur and manganese, for example, it would be entirely out of place to "identify" a number of inclusions as manganese sulphide. On the other hand, if sulphur is present sulphide inclusions must be present. Their constitution will depend, roughly, on the relative amounts of sulphur and of manganese, and of other sulphide-forming metals present. If oxides are present they may safely be assumed to consist of a complex of the oxides of all the metals revealed by the analysis; in particular, it may be concluded that manganese and aluminum will be united with oxygen in preference to sulphur. The presence of silicon generally implies the presence of silicates. An "insoluble residue" suggests

silicates and alumina. The relative amounts of inclusions can also be estimated from the data of analyses, especially if these data include oxygen determinations.

In general, an intelligent estimate on the basis of data of careful chemical analyses, coupled with an examination, preferably at high powers, of a few representative inclusions, will serve to convey a fairly good idea about the nature of the inclusions present.³⁷ The conclusions arrived at will, surely, be more nearly correct than a conclusion based on the results of "standard" identification methods alone.

Thus, following the prescriptions of Campbell and Comstock's method, the author "identified" some 40 per cent of the inclusions in ingot iron to be "lime wash", some 5 per cent manganese oxide or iron carbide, and the balance—manganese silicate.³⁸ This result proved to be 100 per cent wrong. And, at least partly, this was the fault of the method which should be more specific in some of its prescriptions and less definite in many of its conclusions.

Campbell and Comstock's Method and its Modification by the Author

Campbell and Comstock's method merits, nevertheless, especial attention. It is more systematic, straightforward and simple than any other method proposed. No cumbersome gaseous reagents are employed, nor heating of the specimen to temperatures which would involve undesirable tarnishing of the polished surface. To the contrary, the specimen is etched in the same manner as for ordinary metallographic purposes, and, in most instances, even in the same reagents.

In his work on inclusions, described in Chapters II-IV, the author has repeatedly employed etching tests prescribed by Campbell and Comstock, and has had occasion to observe their effect on known inclusions. The results of these tests have already been described.

On the whole Campbell and Comstock's method is good:—to

³⁷Attention must be called to the fact that experience with inclusions is an essential prerequisite for judging them, especially by appearance and association.

³⁸The inclusions in ingot iron properly identified (see Chapt. VI of the author's thesis) are:

| | |
|--|-----|
| Iron oxide (slightly contaminated) | 95% |
| FeO-FeS eutectic | 4% |
| Sulphide rich in Mn (?)..... | 1% |

be serviceable, however, it should be considerably modified. Concentrations of etching reagents should, in all cases, be specified definitely and the use of "strong" or "fairly strong" in this connection avoided. Care should be taken to avoid "identifying" inclusions whose existence in iron, in the pure form, is open to doubt. The results of individual etching treatments should be interpreted, in many instances, with greater caution.

These recommendations as well as other desirable changes have been incorporated in a modified "method", presented in Table III. This modified "method" is far from final and, perhaps, even far from serviceable. It is however, a closer approximation to the truth than the original "method".

8. *The Influence of Inclusions on the Useful Properties of Iron and Steel*

The main practical issue of the problem of inclusions centers about the question: What is the influence of inclusions on the useful properties of the metal? Having had no occasion to secure original experimental evidence on this vital question the author must refrain from discussing it in any detail.

Inclusions and Fatigue Failure. According to most metallurgists inclusions are harmful—harmful in direct proportion to their number, and to the extent to which they are segregated. Failures in steel parts have been repeatedly traced to the presence of inclusions, and the detrimental effects of inclusions on the fatigue resistance of metals has been conclusively demonstrated. (21, 24, 28, 32, 41, 44, 79, 80 and many others).

The reason for this harmful effect of inclusions becomes obvious when principles of the theory of elasticity or the strength of materials are applied to the problem. The edges of inclusions are regions of high stress concentration, and this explains why cracks are found so often to start from inclusions. The formation of a crack, no matter how small, serves to increase the concentration of stress; this in turn facilitates further cracking; this again causes increased stress concentration; and so on, until failure is unavoidable.

The presence of inclusions is especially harmful, therefore, in brittle and hard metals in which cracks are easily started. From what has been said it is further evident that small globular inclu-

sions are least harmful, elongated and continuous shapes, as well as localized aggregates, most dangerous.

Inclusions and "Directional Properties." Not infrequently inclusions are blamed for the "directional properties" of forged steel viz., a weakness in a direction perpendicular to that of rolling or forging. The reason for this effect of inclusions lies again in the highly increased stress concentration which takes effect at the ends of the drawn out inclusions, when the material is pulled in a direction across these inclusions. When pulled lengthwise the stress concentration is insignificant.

A lesson about the influence of inclusions can be learned from the behavior of ingot iron. Charpy bars of rolled ingot iron, when tested in directions parallel and perpendicular to that of rolling, show little, if any, difference in impact strength. Does it not follow that the "directional properties" observed in mild steel (which is ordinarily freer from inclusions than ingot iron) are ascribable primarily to segregation phenomena (leading to a banded structure) rather than the effect of inclusions?

It must be borne in mind, of course, that the oxide inclusions in ingot iron are less plastic at rolling temperatures than sulphide inclusions for example; and, being moreover small, they are elongated much less than the larger and more plastic inclusions in steel. The latter, if sufficiently numerous and sufficiently drawn out, unquestionably do weaken the impact resistance of steel, in the direction of the "grain". The relative importance, then, of inclusions and of dendritic segregation in imparting directional properties will differ considerably for different steels. In general, the dynamic strength of a metal will be affected more seriously by inclusions than the strength under static load.

Inclusions and Corrosion. Inclusions are believed by many to impair the resistance of iron and steel to corrosion. While it cannot be denied that this may be the case, the influence of inclusions in accelerating corrosion is far less serious, in the opinion of the author, than the influence of alloy-forming impurities.

The resistance to corrosion of Armco ingot iron which is essentially free from alloy-forming impurities is a case in point. This iron, as is well known, abounds in inclusions most of which are oxides. And, according to Law (25), oxides are especially prone to accelerate corrosion.

“Oxide of iron differs in one respect from all the other impurities in steel. . . . The difference referred to is the influence exerted by the impurities on the corrosion of steel. . . . If specimens for microscopical examination or freshly filed surfaces are kept side by side in an ordinary room, it will be seen that steels containing oxide begin to show signs of rusting long before the others. . . .”

The findings of Austin (81) are diametrically opposite, and in all probability more nearly correct. Referring to an oxygen-iron alloy studied, he states: “The author believes that the resistance to atmospheric corrosion. . . . of the alloy. . . . will have technical applications.”

Opinions on the subject are, clearly, divided.

Wrought iron is another example of a metal literally crowded with inclusions, yet it is unusually resistant to corrosion.

On the other hand, it is well known that ferrite contaminated by alloy-forming impurities—manganese for example—is attacked by etching reagents much more readily than pure ferrite.

No general conclusions can be drawn on the basis of these rather special examples,—they are, nevertheless, indicative of the fact that inclusions may not be nearly as harmful in inducing corrosion as is held to be the case.

Inclusions and Red-Shortness. Another important effect, largely ascribed to the harmful influence of inclusions, is red-shortness. Iron sulphide, in particular, is held to be responsible for this defect, although it is ascribed, not infrequently, to oxygen, silica and alumina.

Some metallurgists (85, 86, 87) believe copper to be the source of red-shortness; other workers (83) assert that copper actually helps to correct the red-shortness induced by sulphur. Some are inclined to put the blame largely on oxygen (81, 88, 89) others again advance evidence which tends to show that oxygen is harmless (83, 90).

Even in regard to the detrimental influence of sulphur there has been some divergence of opinion; the majority of metallurgists believe, however, that sulphur, in the absence of manganese, is invariably a cause of red-shortness of iron, even if present in quantities barely exceeding some 0.010 to 0.015 per cent.

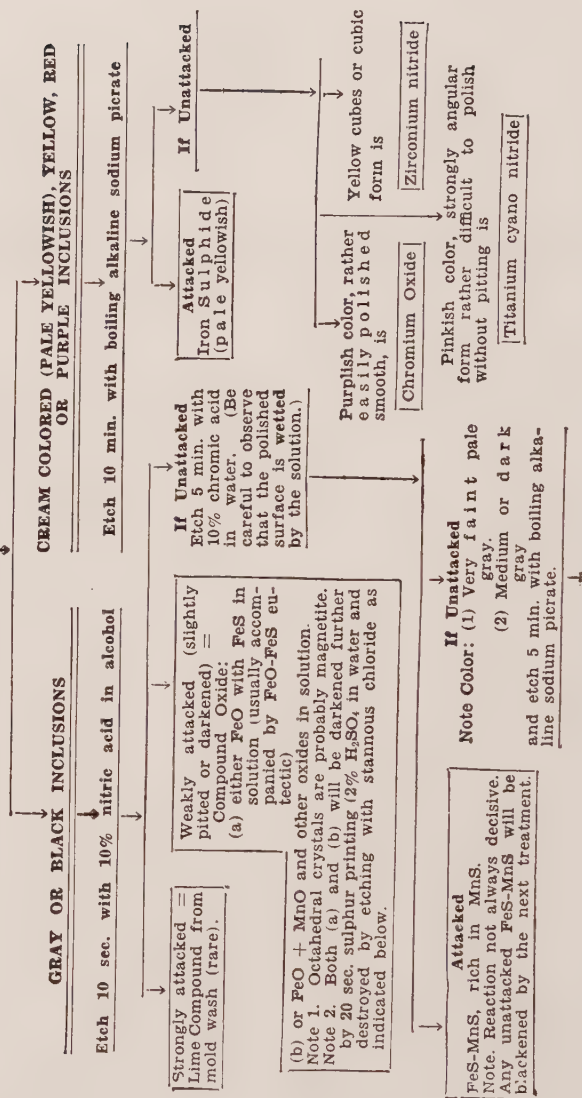
We shall in the following devote our attention primarily to

Table III

METHOD FOR IDENTIFICATION OF INCLUSIONS IN IRON AND STEEL

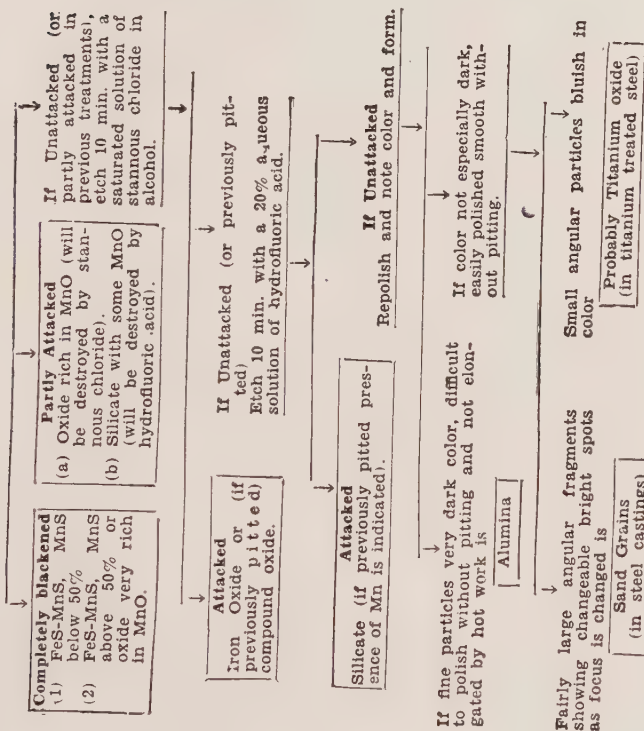
By Campbell and Comstock (Modified by *Wohrman*)

Polish carefully so as to preserve inclusions and project magnified image on ground glass by arc or equally white light without color screen.



this peculiar action of sulphur and examine the mechanism whereby sulphur red-shortness is induced.

Already Le Chatelier (16) pictures the disastrous effect of sulphide inclusions, stating: "It can be readily conceived that. . . networks of sulphide, a substance having very little tenacity and



Supplementary Tests

In all instances check your determinations in the light of the evidence of a careful chemical analysis, and, whenever possible, by other methods, such as:

I. Sulphur printing (for 20 seconds, using a 2% aqueous solution of H_2SO_4):

(1) dissolves all FeS-MnS inclusions.

(2) partly dissolves (pits) FeO containing FeS and oxides of other metals in solution.

(3) leaves unchanged: iron sulphide (pale yellow) pure iron oxide (med. gray) silicates (dark gray)

II. Matweieff's Tests. See A. Sauveur's "Metallography and Heat Treatment of Iron and Steel", pages 512 and 513, 1926.

III. Rohl's Tempering Test for Sulphides. Same reference as in II, page 513.

melting at 980 degrees Cent., will decrease considerably the resistance of the iron in the cold, and completely destroy it when hot."

Today hot-stortness due to sulphur is fairly universally explained by this tendency of the sulphide to form continuous en-

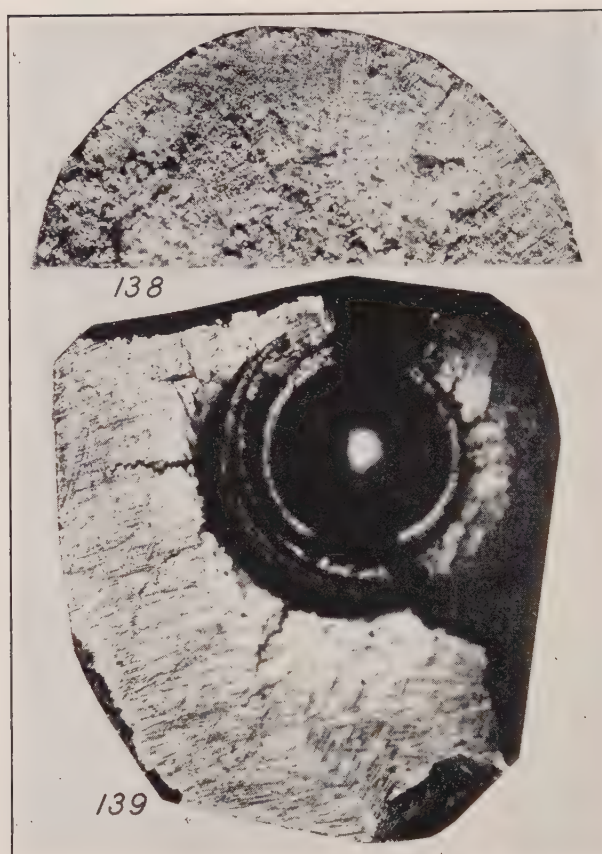


Fig. 138—S-1. (Over 1 Per Cent Sulphur), Broken with a Blow of the Hammer. The Metal Fails Along the Brittle Inter-Dendritic Envelopes of Sulphide. $\times 3\frac{1}{2}$. Fig. 139—S-1. Failure Under the Brinell Test. $\times 3\frac{1}{2}$.

velopes around the “grains” of the metal. The envelopes break up the continuity of the metallic mass and cause, when melting at about 1795 degrees Fahr. (980 degrees Cent.), the falling apart of the metal. At still higher temperatures the molten sulphide is absorbed (dissolved) by the iron which then regains its continuity and plasticity. [Ziegler (36)] Let us examine the accepted ideas critically beginning with fundamental considerations.

Hot-shortness or red-shortness implies lack of plasticity, brittleness, at an elevated temperature, or rather a definite temperature interval, of a pure metal, alloy or aggregate, irrespective of

the plastic qualities of such a metal or aggregate at other temperatures.

The plasticity (also brittleness) of a substance is (like all physical properties of a substance), in the last analysis, a function of the atomic and of the interatomic and intermolecular bonds of the substance, as well as of the conditions of pressure and temperature.

Pure iron is inherently plastic—at all ordinary temperatures and pressures; pure ferrous sulphide inherently brittle, at any rate at atmospheric pressure and room temperature. Consider an aggregate of pure iron and ferrous sulphide at room temperature. The physical properties of an aggregate can be deduced, roughly, from the physical properties of the constituent substances and the structure of the aggregate. In particular, the plasticity of an aggregate of one plastic and one brittle constituent is determined by the predominance and continuity of the plastic constituent. In the present case the plastic iron is clearly, in excess of the brittle sulphide.

But, according to the testimony of many, the continuity of the iron is effectively broken up by envelopes of the sulphide. Deformation of the iron cannot, then, take place without deformation of the sulphide. The latter, being brittle, will not permit of any deformation and will break under the applied stress. Fig. 138 shows how such a metal (S-1) breaks along inter-dendritic surfaces when struck with a hammer. An analogous case is met with in white cast iron which consists of plastic pearlite dendrites separated by brittle cementite fillings and boundaries. A blow will break the metal the fracture exhibiting a distinct dendritic structure (Fig. 137).

The melt S-1, containing over 1 per cent sulphur was found to be so brittle, on account of the continuity of the sulphide inclusions, (Fig. 43) that it failed when a Brinell reading was attempted (Fig. 139). The melt S-3, with 0.125 per cent sulphur (Fig. 56) permitted such a test, however, and was otherwise, too, essentially plastic in the cold. This is obviously explained by the much less pronounced continuity of the sulphide inclusions in this melt. Now, if even 0.125 per cent sulphur fails to provide continuous membranes, how can we expect 0.02 per cent sulphur to accomplish this or even 0.015 per cent sulphur? No one will deny that Arceo in-

got iron is plastic at ordinary temperatures; how could it be plastic if continuous brittle sulphide envelopes (which supposedly cause its red-shortness) were present? Or is it the extreme thinness of these envelopes that makes them less obnoxious?—they are absent, as the writer has had occasion to show repeatedly, for the 0.02 per cent sulphur present in ingot iron is accounted for by isolated inclusions. Yet we continue to refer to continuous membranes in explaining red-shortness!

What happens when we heat sulphide-bearing iron? The author heated the partly distintegrated specimen which failed under the Brinell ball (Fig. 139) to 1470 degrees Fahr. (800 degrees Cent.) and forged it without any difficulty to the thinness of a dime. The sulphide, at elevated temperatures, becomes plastic; the iron is plastic; hence the aggregate of the two is and must be plastic. One would expect this plasticity to increase with increasing temperature and this is actually the case. A discontinuity occurs, however, within a narrow temperature interval in the neighborhood of 1740 degrees Fahr. (950 degrees Cent.), the aggregate suddenly becoming brittle. This temperature interval may well correspond to the fusion point of the Fe-FeS eutectic. But should the presence of this material in discontinuous patches affect the ductility of the metal any more than actual voids would?

There is further this peculiarity. No matter how much a red-short metal is worked either above or below the zone of red-shortness, it will fail when subjected to deformation in that zone. On the other hand, cases are known where alloys containing a complete network of a brittle constituent can be successfully worked after the continuity of this network has been destroyed by careful initial working. Jeffries (86, p. 359), for instance, cites an example of cast steel containing 2.65 per cent of carbon which was successfully worked after "gentle" initial working or "breaking down". The extreme thinness of the hypothetical sulphide network should certainly be conducive to such "breaking down." Yet this cannot be accomplished.

Must we not conclude that the cause of red-shortness is of an entirely different nature than the brittleness induced through the presence of a non-forgeable constituent? The constancy of the temperature interval of hot-shortness for pure iron, the nearness of this interval to the A_3 point, the fact that this interval is lower

for steel for which the A_3 point also is lower;—all this points unmistakably to some connection between red-shortness and the gamma-alpha transformation of iron.

It is instructive, in this connection, to recall the phenomenon of "critical plasticity" at the A_3 point, discovered by Professor Sauveur and Dr. Lee (58, p. 108). Professor Sauveur writes: "When a bar of iron or low carbon steel is heated at the center of its length to a temperature exceeding the A_3 point, and then twisted, the twisting does not occur at the center where the bar is hottest, but at two points equidistant from that center where the bar is undergoing its A_3 transformation."

A study of the photographs of the twisted bars (91) suggests to the author that the point of "critical plasticity" does not occur at the A_3 point proper, but in a region of the iron which just completed its transformation and thus represents alpha iron at the highest temperature of its existence. On both sides of this point the plasticity diminishes:—it diminishes toward the alpha iron side on account of the normal fall of plasticity with temperature; it diminishes toward the gamma iron side, in spite of increasing temperature, because of the admixture to alpha iron of gamma iron which is about to be transformed and is thus at its lowest temperature of existence, the temperature of its minimum plasticity. The rigidity of the metal increases steadily with the increase in gamma iron content until finally a maximum of rigidity is reached when we have one hundred per cent of gamma iron at the temperature of its minimum plasticity. From then on the temperature gradient makes itself felt again and the plasticity of gamma iron gradually increases.

These deductions are supported by recent quantitative measurements of the malleability of iron and steel at high temperatures by Ellis (92). Ellis found that "the allotropic change at A_3 occasioned a distinct increase in the resistance of the metal to plastic transformation," and that when "the temperature of inflexion is reached . . . the austenite suddenly hardens." At about 2550 degrees Fahr. (1400 degrees Cent.), presumably the beginning of the delta change, another break in malleability was observed, the iron acquiring here quite suddenly a highly increased plasticity. Ellis is unquestionably correct in concluding that "a change, the converse of that which occurs in austenite as it approaches the upper critical point (A_3) on cooling, occurs as it approaches A_4 on

heating." His interpretation of the cause of these changes,—a "carbide expansion" at A_3 and "carbide contraction" at A_4 , is less convincing, however.

It is obvious that the changes are attributable, primarily, to the allotropic changes. Gamma iron, on account of its atomic constitution, is less plastic than alpha (or delta) iron, and is in fact "hard" at the lower temperatures of its existence. What is the bearing of these facts on the problem of red-shortness? The author ventures to suggest the following explanation.

The influence—both beneficial and detrimental—of small amounts of alloyed substances on the physical properties of a metal is well known. Gamma iron lacks plasticity in the neighborhood of 1740 degrees Fahr. (950 degrees Cent.). A small amount of alloyed sulphide (and perhaps oxide) emphasizes this lack of plasticity to such an extent that the iron actually disintegrates when worked. At higher temperatures the plasticity of the alloy is increased sufficiently to allow working. At lower temperatures we deal with alpha iron, inherently more plastic.

The beneficial effect of manganese on the red-shortness caused by sulphur (resp. oxygen) can be explained by the lack of solubility of the sulphide (resp. oxide) in gamma iron in the presence of manganese. It may also be that manganese actually helps to improve the plasticity of gamma iron.

The entire problem of red-shortness is thus reduced to the problem of gamma iron or austenite plasticity in the lower temperature regions of its existence, and to the effect on this plasticity of various alloyed elements, and the amount of such alloyed elements.

It may be recalled, in this connection, that certain nickel steels, for example, have a tendency to be red-short (82). This may be accounted for by the influence on the plasticity of austenite of the particular amount of nickel present. And, again, it is manganese which has been found to render these steels forgeable (93).

Inclusions, then, have little influence on the malleability of iron and steel at elevated temperatures. At least not the inclusions which are plastic at hot-working temperatures. Inclusions which are substantially hard at these temperatures, and at the same time sharp-edged, such as alumina and silica, may, however, be ex-

pected to exert some sort of "tearing" action on the weakly plastic metal, thus causing it to break on severe deformation.

Beneficial Influences of Inclusions. We have mentioned, heretofore, only the harmful and undesirable influence exerted by inclusions on the metal that harbors them.³⁹ There is little to be said in their favor.

One may mention, perhaps, that the presence of sulphide in mild steel improves its "free cutting" properties and that the "fiber" created by elongated FeS-MnS inclusions in severely worked steel shapes is supposed to contribute toward the strength of such shapes in a longitudinal direction. It has also been claimed that the presence of oxide inclusions accounts for the unusually favorable enameling qualities of Armco ingot iron.

Conclusions. On the whole, inclusions are harmful and undesirable. The harder the inclusion-bearing metal, the greater the number of inclusions present, the larger their size, the more complete their continuity and segregation, the more dangerous they are. Inclusions, in all instances, lower the fatigue resistance of a metal. Their effect on the "directional properties" of worked material is probably less marked than is generally assumed.

Inclusions play but a secondary role in the importance of their contributions toward the corrodibility of metals, as well as the phenomenon of red-shortness in metals. Alloy-forming impurities should be held responsible for these defects.

9. *The Elimination of Inclusions*

Having considered the inception and birth of inclusions, looked into their behavior and habits, and studied their characteristics and harmful influences, the logical and desirable thing to do would be to write a chapter on their death. This chapter, unfortunately, cannot be written as yet. And it will hardly be written as long as present methods of steel-making continue in use in their existing form.

We make steel by a process which depends on oxidation. Iron oxide dissolved in the molten product will, therefore, invariably be present. Deoxidizers may eliminate most of the iron oxide, but

³⁹The harmful influences which were mentioned are not the only ones. Of those omitted, the well known effect of inclusions on case hardening is, perhaps, the most important. Inclusions, notably oxide inclusions, are the cause of the so-called "soft spots" which are highly undesirable in a good case.

they substitute another oxide (viz., silicates, aluminates) for it, which, ordinarily, is not eliminated before solidification. Worse still, an excess of the deoxidizer may, in some cases, be more harmful to the metal than the inclusions it was meant to correct. The best we can do, at the present, is to limit the nuisance of inclusions by wisely directing our furnace and ladle operations and by choosing a harmless deoxidizer which, at the same time, is least liable to contaminate the steel with its oxidation products, i.e., a deoxidizer whose oxidation products have a strong tendency to escape from the metal and whose products, if entangled in the metal, will occur in relatively harmless form—the form of tiny globules evenly distributed.

Having performed no experiments in this direction, the author avoids, on purpose, to be more specific in his recommendations.

It is clear that inclusions once formed are with the metal to stay and that nothing short of remelting will exterminate them. Inclusions cannot be remedied; they must be prevented.

Cleanliness of materials and care of operations will go a long way toward accomplishing this. Electric steel is a point in case.

Scientifically controlled cooling and solidification conditions, as yet largely unspecified, will afford further relief. A prolonged period of fluidity after the last additions are made will unquestionably help the suspended matter to leave the metal. If this be followed by slow solidification in vacuo, gases would also be eliminated. To correct segregation which would be favored by quiet slow cooling, solidification should not be allowed to take place undisturbedly. The metal should be worked by some means, already while still essentially fluid.

There are other possibilities. Many of them are impracticable today, many of them imply refinements as yet uncalled for. They may be called for tomorrow and we should be ready for them.

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